Final Report

**AIR QUALITY TECHNOLOGY DEVELOPMENT NEEDS:
DIESEL NOx EMISSION REDUCTION TECHNOLOGIES**

Prepared for

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Texas Senate Bill 5 (2001 session) established the Texas Emission Reduction Plan (TERP) to provide financial incentives for reducing emissions from on-road and off-road motor vehicles. The majority of the resources for this program are dedicated to reducing NOx emissions from on-road and off-road diesel engines. Additionally, SB 5 created the Texas Council on Environmental Technology (TCET). The purpose/charge of TCET is to enhance the entrepreneurial and inventive spirit of Texans to assist in developing solutions to air, water, and waste problems by identifying and evaluating new technologies and seeking the approval of the United States Environmental Protection Agency (USEPA) for and facilitating the deployment of those technologies; and assisting the commission and the United States Environmental Protection Agency in the process of ensuring credit for new, innovative, and creative technological advancements. To assist the Council in developing a long range plan for catalyzing the deployment of existing and new emissions reduction technologies, this work performed a critical assessment of air quality technology development needs including a review of the status of existing and emerging technologies and characterizing of emissions from source types and emissions reduction potential by source categories performed for the two most important nonattainment areas of Dallas-Ft. Worth and Houston-Galveston. This report summarizes the work of a project funded by the TCET in response to the TCET project, "Developing a Critical Assessment of Air Quality Technology Development Needs."

This report reviews the available and emerging NOx emission reduction strategies for diesel engines, their current level of development, including official emission reduction verification status, their cost and cost effectiveness, the applicable emissions in the Houston-Galveston (HGA) and Dallas-Ft. Worth (DFW) nonattainment areas to which these technologies could be applied, and recommendations for improvement of the development of commercializing emission reduction technologies. Recommendations are suggested for the improvement of the overall goals of Senate Bill 5, the TERP, and other incentive programs.

Technologies exist to reduce diesel engine emissions. These include cleaner burning fuel options, engine/vehicle replacement, and retrofit of existing engines with emissions reduction technologies. Several emission reductions for fuel options exist to reduce emissions, including funded TERP projects for fuel/water emulsions and other unfunded options for additional diesel fuel reformulation. The most prevalent TERP project, and for the analogous California Carl Moyer program, is the early retirement of vehicles or equipment or the replacement of current engines with cleaner diesel or compressed or liquefied natural gas (CNG/LNG) engines. Retrofit options for current equipment include adding equipment to humidify the intake air, modifying fuel injection timing with additional particulate traps, applying exhaust gas recirculation (EGR), lean NOx reduction catalysts, and selective catalytic reduction (SCR). Additional retrofit options applying nascent technologies of NOx adsorbers or plasma NOx reduction catalysts may become available in subsequent years.

The verification of many of these technologies has lagged because the verification process is both cumbersome and costly. For instance, the USEPA has not verified any NOx reduction technologies, though it has published best estimates for the emission reductions from the use of cleaner fuel options. The USEPA has verified to date only particulate control technologies, and the California Air Resources Board (ARB) has only begun to certify emission control

technologies. For example, ARB has only verified one injection modification control technology and has issued interim verification for a lean NOx reduction catalyst to reduce emissions. Under Senate Bill 5, TERP has funded an EGR retrofit project that does not currently have verification status, but presumably will have verification by its conclusion. TCET has funded a project to gain EPA verification for a lean NOx control technology. TCET can continue to accelerate the verification of new technologies either through additional grants or by working more closely with USEPA and ARB. But because the introduction of retrofit options are burdened by the verification process, the most straight-forward and widely employed NOx reduction methodology is to accelerate the turnover of diesel engines to those meeting significantly lower emission standards.

The cost and cost effectiveness of NOx emission reduction strategies for diesel engines was determined using the official TERP method, an approach where the cost of the project is converted to an annual cost benefit over the life of the project divided by the annual benefit, or as a one-year cost effectiveness where the total cost of the project is divided by the benefit in the attainment year. The one-year cost effectiveness is useful for determining the total cost of a near term air quality goal. The TERP annualized cost effectiveness for the technologies reviewed in this report range from $1,000 to well over the $13,000 per ton of NOx reduced limit for TERP eligibility. Typically, the annualized cost effectiveness for TERP projects is about $10,000 per ton of NOx reduced while the comparable California Carl Moyer program has experienced better cost effectiveness in the range of $3,000 to $6,000 per ton of NOx reduced, on average, with best estimates at about $19,000 per ton of NOx reduced for the one-year cost effectiveness. Off-road projects tend to be more cost-effective than on-road projects because base emissions rates for off-road engines are higher than those for on-road vehicles resulting in greater mass emission reductions per engine.

An emission inventory summary was presented, which outlined the NOx emissions eligible for TERP funded projects and highlight those areas where TCET could provide assistance. The off-road emissions were derived from the State Implementation Plans (SIPs) for the HGA and DFW nonattainment areas. The on-road emissions estimates used the most recent calculations based on the new MOBILE6 model, which was not available when the SIPs were developed but will be used in future SIP revisions. In HGA, 117 tons per day (tpd) of NOx emissions (54 tpd from heavy-duty on-road diesel vehicles above 10,000 pounds gross vehicle weight and 63 tpd from off-road diesel engines above 50 horsepower) are eligible for TERP funded projects. By expanding the definition of TERP-eligible to include other heavy-duty diesel vehicles (6 tpd), heavy-duty gasoline vehicles (16 tpd), smaller off-road diesel engines (3 tpd), off-road spark-ignition engines (9 tpd), and stationary internal combustion (IC) engines (unknown emissions), the available emissions in HGA for emission reduction projects can be increased by more than 30%. Similar estimates for DFW show that the currently TERP eligible NOx emissions are 115 tpd and additional sources can increase the available emissions by more than 40%. TCET could therefore consider technologies that apply to these sources, which are ignored by TERP and other emission reduction programs.

Recommendations for improvement of the TCET and other Senate Bill 5 incentive programs include adding USEPA verification assistance to jump start significant emission reduction technologies, lowering the minimum emission reduction for retrofit to below 30%, and expanding the eligible emission sources to include more on-road and off-road equipment types.

The Texas Council on Environmental Technology (TCET) could assist various technologies by expanding funding to assist in the verification process. In the past funding cycle, TCET has provided this type of funding to assist lean NOx reduction and TERP has funded a large project for an EGR retrofit project, which must include verification as an overall goal of that project. Technologies developing to meet the 2007 on-road diesel engine emission standards to reduce NOx emissions by up to 90% (including SCR, NOx adsorbers, and plasma catalytic reduction) provide additional opportunities to assist in developing retrofit options. These technologies used to meet new engine emission standards are likely also the most cost-effective retrofit technologies to promote emission reductions from existing engines and could benefit from resources to enable their development and verification.

Two existing emission reduction technologies, fuel injection modifications and lean NOx catalysts, would be declared ineligible under the TERP requirement that such technologies must reduce emissions by more than 30%. These technologies have been verified by the California ARB, and therefore might reasonably be expected to obtain USEPA verification. If the 30% reduction minimum is not lowered, then these technologies would be effectively ignored and attention should shift to focus on technologies expected to be eligible for funding.

Currently available technologies may be applied to vehicle or equipment that is not currently eligible for TERP funding. These include smaller diesel engines, Class 2b (gross vehicle weight ratings of 8,500 to 10,000 lbs) vehicles, and stationary diesel engines. Feasible Technologies for the currently eligible engine types could be applied to produce additional emission reductions.

Additional technologies eligible for TCET grants but unable, at this time, for TERP funding could be considered under an expanded definition of eligible emission sources. Examples include California Carl Moyer program projects for electrification of certain equipment types such as agricultural pumps, use of fuel or solar cells for applicable equipment types, retrofit of uncontrolled spark-ignition engines with a NOx reduction catalyst (i.e., found on light-duty vehicles), and selective use of turbines instead of IC engines. The expanded emissions sources would include Class 2b heavy-duty vehicles, small diesel engines (less than 50 horsepower), on-road and off-road spark-ignition engines, and stationary IC engines. TCET could fund such cost effective projects, but TERP has more resources available to affect more substantial emission reductions.

1.0 INTRODUCTION

Texas Senate Bill 5 (2001 legislative session) established the Texas Emission Reduction Plan (TERP) to provide financial incentives for reducing emissions from on-road and nonroad motor vehicles. Additionally, SB 5 created the Texas Council on Environmental Technology (TCET). The purpose/charge of TCET is to enhance the entrepreneurial and inventive spirit of Texans to assist in developing solutions to air, water, and waste problems by identifying and evaluating new technologies and seeking the approval of the United States Environmental Protection Agency (USEPA) for and facilitating the deployment of those technologies; and assisting the commission and the United States Environmental Protection Agency in the process of ensuring credit for new, innovative, and creative technological advancements (http://www.tnrcc.state.tx.us/oprd/sips/leg_report.html). To assist the Council in developing a long range plan for catalyzing the deployment of existing and new emissions reduction technologies, the work reported here provides a critical assessment of air quality technology development needs. This includes a review of the status of existing and emerging technologies, and characterizing of emissions from source types and emissions reduction potential by source categories. This characterization was performed for the two largest nonattainment areas of Dallas-Ft. Worth and Houston-Galveston.

This report summarizes the work of a project funded by the TCET in response to the TCET project, "Developing a Critical Assessment of Air Quality Technology Development Needs." This report reviews the available and emerging NOx emission reduction strategies for diesel engines, their current level of development including official emission reduction verification status, their cost and cost effectiveness, the applicable emissions in the Houston-Galveston (HGA) and Dallas-Ft. Worth (DFW) nonattainment areas to which these technologies could be applied, and recommendations for improvement of the development of commercializing emission reduction technologies. Recommendations are suggested for the improvement of the overall goals of Senate Bill 5, the TERP, and other incentive programs.

Because the majority of the resources provided by Senate Bill 5 were dedicated to the TERP, TCET can assist and develop technologies for use in the TERP, so it is helpful to understand the goals and restriction under current TERP guidelines. The guidelines for the TERP were laid out in Senate Bill 5 (Rule Log 2001-025b-114-AI) and later clarified in TERP Guidelines for Emission Reduction Incentive Grants (October, 2001). It was stated that projects must meet the following conditions:

- That 75% of the activity occur within the eligible areas of Houston-Galveston and Dallas-Ft. Worth nonattainment areas
- Retrofit projects must result in at least a 30% N0x reduction
- The cost effectiveness must be less than $13,000 per ton N0x (lifetime cost)
- Only diesel engines greater than 50 hp for off-road vehicles, and gross vehicle weight ratings (GVWR) greater than 10,000 lbs for on-road vehicles are eligible for funding.

According to the legislation the money is to be distributed in this way:

- 72% for diesel emissions reduction programs
  - Not more than 3% of this 72% for infrastructure projects

       ○ Not more than 15% of this 72% for on-road diesel purchases
- 10% for light-duty purchases and lease incentives
- 7.5% for energy efficiency programs
- 7.5% for new technology and research (TCET), and
- 3% for administration

The purpose of this work was to review the diesel technologies, their maturity, and relative cost and cost effectiveness. This report then addresses the majority of the effort of the TERP, how TCET could assist by funding research and development of new and emerging technologies for the TERP, and suggests additional emission reduction technologies that could be funded under the current TCET charge or under an expanded TERP. The following chapters address the topics associated with the work reviewing Diesel Emission Reduction Technologies:

- A review of technologies that can be applied to diesel engines to reduce emissions.
- A review of the EPA process used to gain emissions reduction/technology verification, and status of verification of the emission reduction technologies reviewed in Chapter 2.
- Reported costs and cost effectiveness estimates for the emission reduction technologies reviewed in Chapter 2.
- Summary of the mobile source emission inventories of the Houston-Galveston and Dallas-Ft. Worth nonattainment areas, and the potential for emission reductions projects.
- Summary and Recommendations.

2.0 BACKGROUND

2.1 INTRODUCTION

The Federal Clean Air Act includes explicit instructions regarding designating certain counties as those that do not attain the National Ambient Air Quality Standards (NAAQS). These are generally referred to as "non-attainment areas". By applying these rules and instructions, the Houston-Galveston area fell in the non-attainment category for the NAAQS for ozone, and thus requires some stringent measures to ensure the health of citizens living in this area, as well as ensuring compliance with Federal regulations requiring minimum standards for healthy air. Developing and implementing new emission controls for a variety of economic sectors is therefore encouraged in this all-important effort to comply with the Federal mandates. The example established by the Houston-Galveston area is not unique in the State of Texas. Many other metropolitan areas with large population density suffer the same symptoms of the Houston-Galveston areas, but perhaps at lesser degrees of severity.

The Texas Council on Environmental Technology (TCET) has been established to act as the catalyst for identifying new emission control technologies and facilitating their implementation. In so doing, TCET will assist the U. S. EPA in assessing the worth of new technologies and expedite the assignment of appropriate emissions reduction potential credits to these technologies. To meet this new challenge, TCET has commissioned a study of the various sources of emissions in the State of Texas. This study will estimate the contribution of these sources to the State emission inventory. It will then develop a comprehensive list of technical solutions, and then make recommendations on the prioritization of the implementation of these solutions to achieve the largest return in reducing these emission inventories at a minimum of cost and pubic inconvenience.

The work reported here addresses the current state of control technology as it might be applied to one sector of the emissions inventory that contributes to ozone forming precursors: heavy-duty diesel engines (HDDE). We first provide an extensive background of the regulatory environment, past and present, as well as diesel equipment combustion characteristics. We then we provide a very thorough discussion of methods that have been and may be used in the future for the reduction of air pollutant emissions formed in the diesel combustion process.

2.2 THE REGULATORY ENVIRONMENT

Heavy-duty diesel engines are used in many applications such as large trucks, school buses, marine, and locomotives. For large trucks in particular, HDDEs have proven to be reliable, durable, and very fuel-efficient. In fact, because of these qualities, HDDEs play a central role in the transportation of goods and materials in Texas, the United States, and around the world. Therefore, HDDEs are essential for a strong economy.

Diesel engines emit extremely low levels of carbon monoxide and unburned hydrocarbon emissions. This fact is based mainly on their heterogeneous combustion that is characterized with high air-to-fuel (A/F) ratios. Their combustion efficiency is extremely high and consequently converts their hydrocarbon fuel to mostly carbon dioxide and water. However, because they power vehicles that can travel almost twice as far as their gasoline-powered counterparts, they have the ability to reduce the total man-made CO_2 contribution to the environment (see Figure 2-1). Diesel engines, however, have traditionally contributed higher

levels of nitrogen oxides and particulate matter to the environment. This problem stems from the fact that, until the present time, diesels have not used an aftertreatment system equivalent to the three-way catalyst in gasoline engines. Compared to gasoline-fueled automobiles and light-duty trucks, HDDEs have significantly lagged behind with respect to using aftertreatment-based emission control systems. This is primarily because regulatory agencies have acknowledged that HDDEs emit relatively low levels of carbon monoxide and unburned gaseous hydrocarbons and waived tight control because of their superior fuel economy. However, in recent years, the "benefits" of HDDEs have been overshadowed by the increase in their relative contribution of NO_x emissions to the overall Texas State inventory and by their potential for causing cancer through the emissions of particulate matter. In addition, particulate matter has long been suspect of causing respiratory diseases and/or aggravating the condition of those who suffer from these diseases. For instance, the California Air Resources Board (ARB) identified diesel particulate matter (PM) as a toxic air contaminant in 1998.
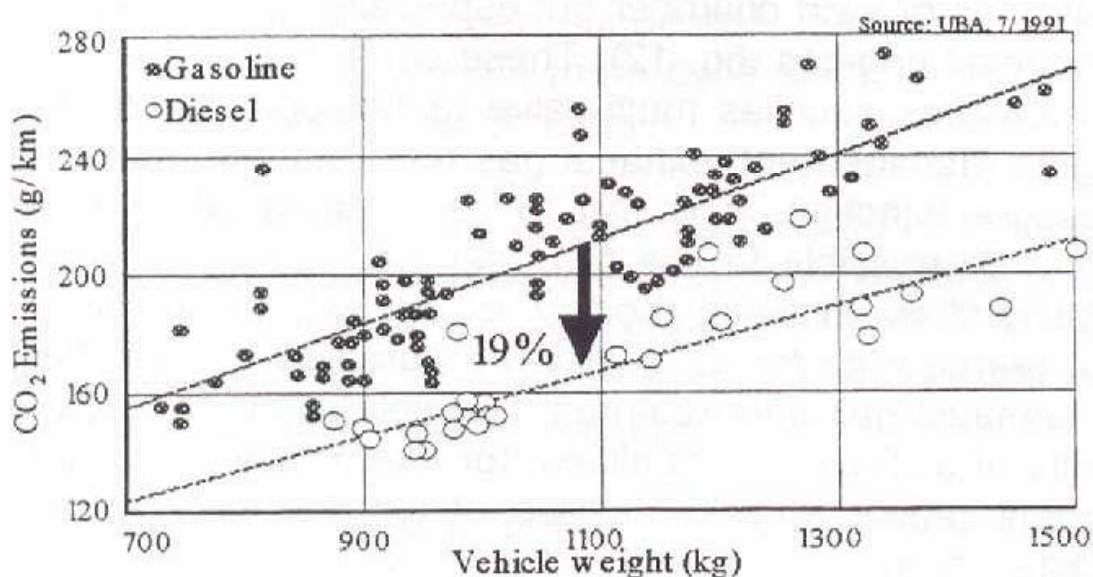
Figure 2-1. Carbon dioxide emission comparison – gasoline vs. diesel.

In October of 2000, the United States Environmental Protection Agency (U.S. EPA) adopted a rule that reaffirmed emission standards for 2004 and subsequent model year HDDEs[1]. This rulemaking also included supplemental test procedures required for certification in addition to the existing Federal Test Procedure (FTP)[2].

Today, the industry is well on the way to developing aftertreatment technologies for diesel engines. Extensive development efforts are being made to develop NO_x aftertreatment technologies. The most prominent of these technologies are: NO_x adsorbers that are vigorously backed by the U. S. EPA, and the urea selective catalytic reduction. For PM, diesel particulate filters have been developed over the last two decades and recent efforts are quite promising for their inclusion in serial production starting with the 2007 model year engines. Encouraged by these developments the U.S. EPA, in January of 2001, followed the 2004 Final Rule with another rule to reduce emission standards for 2007[3] and subsequent model year heavy-duty engines, including both spark-ignited (e.g., gasoline-fueled) and compression-ignited (e.g., diesel-fueled) engines. These emission standards represent a 90 percent reduction of NO_x emissions, 72 percent reduction of non-methane hydrocarbon (NMHC) emissions, and 90 percent reduction of PM emissions compared to the 2002/2004 emission standards (see Figure 2-2).

The 2007 Final Rule is technology forcing since setting these emission standards would require aftertreatment-based technologies. The 2007 Final Rule is a reminder of the regulations which first required the use of catalytic converters on gasoline-fueled automobiles and light-duty trucks in the mid 1970s. The 2007 Final Rule will also be a "systems" approach in the sense that it requires new fuel standards having less sulfur content, engine controls that are in harmony with those of the aftertreatment devices, and perhaps using lube oil formulations that are friendly to the auxiliary emission control devices.
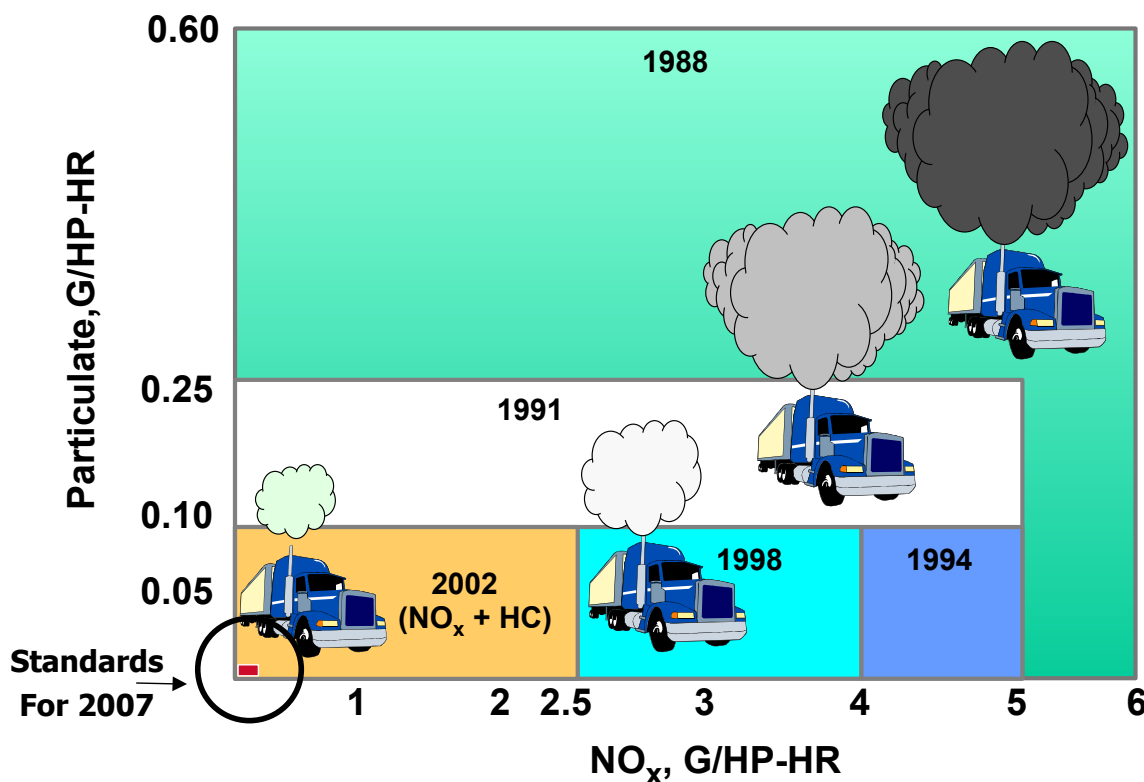
Figure 2-2. Heavy-duty federal emission standards. Grams per horsepower-hour (G/HP-HR).

2.3 DIESEL ENGINES AS A SOURCE OF EMISSIONS

Heavy-duty diesel motor vehicles, with a gross vehicle weight rating (GVWR) of 14,001 pounds and greater, are considered major contributors to the Texas inventory of several key air pollutants including NO_x, reactive organic compounds (ROG), and PM. Both NO_x and ROG are believed to be precursors to ozone. Ozone has long been a concern because of its adverse impact on human health. NO_x alone can also be harmful to humans by aggravating common respiratory illnesses and even prematurely aging lung tissue. NO_x can also be transformed in the atmosphere to nitrate, a form of PM that can cause lung disease and premature death. Further, in August of 1998, California identified diesel PM as a toxic air contaminant.

While catalytic converters have been required on passenger cars for over 30 years, diesel exhaust from HDDEs is released directly into the atmosphere without the benefits of a device equivalent to the 3-way catalyst. Currently, there are many demonstration projects ongoing

worldwide to show the effectiveness of heavy-duty diesel auxiliary emission control devices (aftertreatment). Additionally, improvements to the effectiveness of these devices are ongoing.

This report will apply to HDDEs and medium-duty diesel engines (MDDE). The technologies discussed in this report will apply directly to these two categories of engines in the transportation sector. Some of these technologies will also apply to many diesel engine stationary applications.

2.4 TECHNOLOGY

a. Heavy-Duty Diesel-Cycle Engines

Diesel-cycle engines use compression to ignite the fuel as a basis for their combustion system. By contrast, spark-ignited engines typically use a spark plug to ignite the fuel. Generally, combustion in diesel engines is considered heterogeneous i.e., the fuel is not completely and homogeneously mixed with the combustion air. This combustion system is also in contrast with the spark-ignited combustion process since combustion in this powerplant is said to be homogeneous. This term means that the fuel is almost evenly and perfectly mixed with the combustion air. Combustion usually starts at the spark plug and proceeds quickly through the homogeneous charge until it is completely consumed. This process is quite fast when compared to diesel combustion. In diesel combustion, fuel is injected in hot compressed air. Fuel droplets on the edge of the spray extract heat from the surrounding hot air and in turn evaporate. Evaporated fuel mixes with the hot air and once the auto-ignition temperature is reached, combustion occurs. The progress of the combustion process depends on the rate of fuel evaporation and mixing, which usually requires a more extended time to complete than in the spark-ignited engine.

Combustion in spark-ignited engines proceeds along a flame front that travels quickly through the combustion chamber. NO_x emission is formed along that flame front due to the high temperature reached along that flame front. In diesel combustion, the mechanism for NO_x formation is somewhat more involved. However, as fuel evaporates along the periphery of the jet spray, mixing will take place as previously described.   Once the auto-ignition temperature is reached, combustion starts and NO_x usually forms in the mixed portion of the fuel as long as high combustion temperatures are present. The added air present in large measure in the combustion chamber of lean burning diesels moderates the extreme combustion temperatures and therefore, NO_x formation. In fact, if one considers engine-out NO_x emissions of both combustion systems, we would find that diesel engines produce less engine-out NO_x than their equivalent spark-ignited engines.   However, using 3-way catalyst technology for the spark-ignited engine has marvelously helped achieve very low NO_x emissions that seem impossible for diesel engines to match. Establishing extremely low emission limits on diesel engines has increased the effort to find an equivalent to the 3-way catalyst solution for the diesel engine.

b. Diesel Engine Emissions

Unlike Otto-cycle (spark-ignited) engines, a typical diesel-cycle engine inducts a large amount of air into the combustion chamber. This air remains constantly in excess of the chemically

ideal stoichiometric air-to-fuel ratio. Power from a diesel engine, is controlled by regulating the amount of fuel that is injected into the combustion chamber.

Since air in the combustion chamber of a diesel engine is always in excess of the chemically correct ratio required for complete combustion, hydrocarbon and carbon monoxide emissions are extremely small. The primary pollutants of concern from diesel engines are NO_x and PM, since both are harmful to human health. Evaporative emissions from diesel engines are not significant since diesel fuel has a low vapor pressure and thus, a low evaporation rate. In addition to the PM emissions resulting from incomplete combustion of fuel, lubrication oil entering the cylinder contributes to the overall PM emissions.

Another source of emissions from a diesel engine is the crankcase. Crankcase emissions are similar to exhaust emissions. These emissions result when the combustion gases "blow by" the piston rings into the crankcase. Consequently, these gases are vented to reduce the pressure in the crankcase. Currently, venting crankcase emissions to the ambient air is permitted in all on-highway HDDEs equipped with turbochargers, which is essentially the majority of them. Efforts at the regulatory agencies would lead to recirculating crankcase gases back into the combustion chamber, as is currently done in spark-ignited engines.

2.5 EMISSION STANDARDS AND TEST PROCEDURES[4]

The following emission standards apply to new diesel engines used in heavy-duty highway vehicles. The current federal definition of a compression-ignition (diesel) engine is based on the engine cycle, rather than the ignition mechanism, with the presence of a throttle as an indicator to distinguish between diesel-cycle and otto-cycle operation. Regulating power by controlling the fuel supply in lieu of a throttle corresponds with lean combustion and the diesel-cycle operation (this allows the possibility that a natural gas-fueled engine equipped with a spark plug is considered a compression-ignition engine).

Heavy-duty vehicles are defined as vehicles of gross vehicle weight rating (GVWR) of above 8,500 lbs in the federal jurisdiction and above 14,000 lbs in California (model year 1995 and later). Diesel engines used in heavy-duty vehicles are further divided into service classes by GVWR, as follows:

- Light heavy-duty diesel engines: $8,500 < $ **LHDDE** $ < 19,500$ $(14,000 < $ **LHDDE** $ < 19,500$ in California, 1995+)

- Medium heavy-duty diesel engines: $19,500 \leq $ **MHDDE** $ \leq 33,000$

- Heavy heavy-duty diesel engines (including urban bus): **HHDDE** $ > 33,000$

Under the federal light-duty Tier 2 regulation (phased-in beginning 2004) vehicles of GVWR up to 10,000 lbs used for personal transportation have been re-classified as "medium-duty passenger vehicles" (MDPV - primarily larger SUVs and passenger vans) and are subject to the light-duty vehicle legislation. Therefore, the same diesel engine model used for the 8,500 - 10,000 lbs vehicle category may be classified as either light- or heavy-duty and certified to different standards, depending on the application.

Current federal regulations do not require that complete heavy-duty diesel vehicles be chassis certified, instead requiring certification of their engines (as an option, complete heavy-duty diesel vehicles under 14,000 lbs can be chassis certified). Consequently, the basic standards are expressed in grams per horsepower-hour and require emission testing over the EPA transient FTP engine dynamometer cycle (however, chassis certification may be required for complete heavy-duty gasoline vehicles with pertinent emission standards expressed in g/mile). Additional emission testing requirements, first introduced in 1998, included the following:

- Supplemental Emission Test (SET)

- Not-to-Exceed (NTE) limits

These tests were introduced for the companies that signed the 1998 Consent Decrees between the EPA and engine manufacturers for the period 1998 - 2004. Federal regulations require the supplemental testing from all engine manufacturers effective 2007. In California, the tests are required for all engines effective model year 2005.
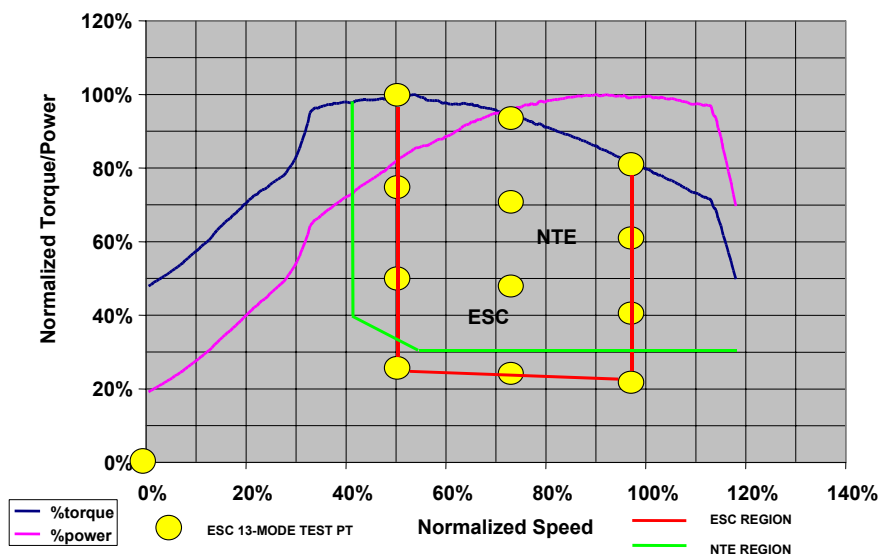
Figure 2-3. Euro III-type steady-state test points and NTE region.

The SET is a 13-mode steady-state test that was introduced to help ensure that heavy-duty engine emissions are controlled during steady-state type driving, such as a line-haul truck operating on a freeway. The test is based on the European 13-mode OICA (Organisation Internationale des Compagnies d'Automobile), which is known in the US as the "Euro III" cycle. This test cycle is described by the test points [circles labeled European Schedule Cycle (ESC) and defined by engine torque and speed] shown in Figure 2-3 where the emissions at each point is individually time weighted to provide an average emission rate. Figure 2-3 also shows typical diesel engine performance with regard to torque and power normalized to the maximum of each and engine speed normalized to the rated engine speed typically reported in revolutions per minute.

The NTE limits have been introduced as an additional instrument to make sure that heavy-duty engine emissions are controlled over the full range of speed and load combinations commonly experienced in use (paid service). The NTE approach establishes an area (the "NTE zone")

under the torque curve of an engine where emissions must not exceed a specified value for any of the regulated pollutants. As shown in Figure 2-3, the NTE region of engine operation is similar but encompasses more engine operation than the region encompassed by the ESC test points but does not include the low torque operation or idle points of the ESC test.

The NTE test procedure does not involve a specific driving cycle of any specific length (mileage or time). Rather it involves driving of any type that could occur within the bounds of the NTE control area, including operation under steady-state or transient conditions and under varying ambient conditions. Emissions are averaged over a minimum time of thirty seconds and then compared to the applicable NTE emission limits.

Model Year 1987-2003[4]

Model year 1988-2003 US federal (EPA) and 1987-2003 California (ARB) emission standards for heavy-duty diesel truck and bus engines are summarized in the following tables. Applicable to the 1994 and following year standards, sulfur content in the certification fuel has been reduced to 500 ppm by weight.

Table 2-1. EPA emission standards for heavy-duty diesel engines, g/bhp·hr.

Year	HC	CO	NO$_x$	PM
Heavy-Duty Diesel Truck Engines				
1988	1.3	15.5	10.7	0.60
1990	1.3	15.5	6.0	0.60
1991	1.3	15.5	5.0	0.25
1994	1.3	15.5	5.0	0.10
1998	1.3	15.5	4.0	0.10
Urban Bus Engines				
1991	1.3	15.5	5.0	0.25
1993	1.3	15.5	5.0	0.10
1994	1.3	15.5	5.0	0.07
1996	1.3	15.5	5.0	0.05*
1998	1.3	15.5	4.0	0.05*

* - in-use PM standard 0.07

Table 2-2. California emission standards for HDDE, g/bhp·hr.

Year	NMHC*	THC**	CO	NO$_x$	PM
Heavy-Duty Diesel Truck Engines					
1987	-	1.3	15.5	6.0	0.60
1991	1.2	1.3	15.5	5.0	0.25
1994	1.2	1.3	15.5	5.0	0.10
Urban Bus Engines					
1991	1.2	1.3	15.5	5.0	0.10
1994	1.2	1.3	15.5	5.0	0.07
1996	1.2	1.3	15.5	4.0	0.05

* Nonmethane hydrocarbon
** Total hydrocarbon

Useful Life and Warranty Periods[4]

Compliance with emission standards has to be demonstrated over the useful life of the engine, which was adopted as follows (federal & California):

- LHDDE - 8 years/110,000 miles (whichever occurs first)

- MHDDE - 8 years/185,000 miles

- HHDDE - 8 years/290,000 miles

Federal useful life requirements were later increased to 10 years, with no change to the above mileage numbers, for the urban bus PM standard (1994+) and for the NO_x standard (1998+). The emission warranty period is 5 years/100,000 miles (5 years/100,000 miles/3,000 hours in California), but no less than the basic mechanical warranty for the engine family.

Clean Fuel Fleet Program[4]

Table 2-3 shows a voluntary Clean Fuel Fleet (CFF) emission standard. It is a federal standard that applies to 1998-2003 model year engines, both compression-ignition and spark-ignition, over 8,500 lbs GVWR. In addition to the CFF standard, vehicles must meet applicable conventional standards for other pollutants.

Table 2-3. Clean Fuel Fleet program for heavy-duty SI and CI engines, g/bhp·hr.

Category*	CO	NMHC+NO_x	PM	HCHO**
LEV (Federal Fuel)		3.8		
LEV (California Fuel)		3.5		
ILEV	14.4	2.5		0.050
ULEV	7.2	2.5	0.05	0.025
ZLEV	0	0	0	0

* LEV - low emission vehicle; ILEV - inherently low emission vehicle; ULEV - ultra low emission vehicle; ZEV - zero emission vehicle
** Formaldehyde

Model Year 2004 and Later[4]

In October 1997, EPA adopted new emission standards for model year 2004 and later heavy-duty diesel truck and bus engines. These standards reflect the provisions of the Statement of Principles (SOP) signed in 1995 by the EPA, California ARB, and the manufacturers of heavy-duty diesel engines. The goal was to reduce NO_x emissions from highway heavy-duty engines to levels approximately 2.0 g/bhp·hr beginning in 2004. Manufacturers have the flexibility to certify their engines to one of the two options shown in Table 2-4.

Table 2-4. EPA emission standards for MY 2004 and later HDDE, g/bhp·hr.

Option	NMHC + NO_x	NMHC
1	2.4	n/a
2	2.5	0.5

All emission standards other than NMHC and NO_x applying to 1998 and later model year heavy-duty engines (Table 2-1) will continue at their 1998 levels.

EPA established a revised useful engine lives, with significantly extended requirements for the heavy heavy-duty diesel engine service class, as follows:

- LHDDE - 110,000 miles/10 years
- MHDDE - 185,000 miles/10 years
- HHDDE - 435,000 miles/13 years/13,000 hours (but not less than 290,000 miles)

The emission warranty remains at 5 years/100,000 miles.

The federal 2004 standards for on highway trucks are harmonized with California standards, with the intent that manufacturers can use a single engine or machine design for both markets. However, California certifications for model years 2005-2007 additionally require the Supplemental Emission Test and NTE limits of 1.25 times the FTP standards. California also adopted a different standard for urban bus engines.

Consent Decree[4]

In October 1998, a court settlement was reached between EPA, Department of Justice, California ARB and six engine manufacturers (Caterpillar, Cummins, Detroit Diesel, Volvo, Mack Trucks/Renault and Navistar) over the issue of high NO_x emissions from heavy-duty diesel engines during certain driving modes. Since the early 1990s, manufacturers used engine control software that caused engines to switch to a more fuel-efficient (but higher NO_x) driving mode during steady highway cruising. The EPA considered this engine control strategy an illegal "emission defeat device".

Provisions of the Consent Decree included the following:

- Civil penalties for engine manufacturers and requirements to allocate funds for pollution research

- Upgrading existing engines to lower NO_x emissions

- Supplemental Emission Test (steady-state) with a limit equal to the FTP standard and NTE limits of $1.25 \times$ FTP (with the exception of Navistar)

- Meeting the 2004 emission standards by October 2002, 15 months ahead of time

California Urban Bus Standard (2002)[4]

This section is included in the report as an example of a model Texas can follow in its effort to control emissions from the transportation sector. In February 2000, CARB adopted a new regulation to reduce emissions of NO_x and PM from urban transit buses. The rule includes a

number of components that affect both engine manufacturers and bus fleet operators. Fleet operators have to choose between a "diesel path" and an "alternative fuel path" for their future bus procurements. The alternative fuel path requires that 85 percent of buses purchased, or leased each year through model year 2015 are fueled by alternative fuels. Transit operators who stay on the diesel path can purchase diesel fueled buses, but are required to follow a more aggressive emission reduction schedule. When the regulation is fully implemented, buses on both paths will produce the same near-zero emission levels.

The regulation provides numerous detailed provisions and schedules, which can be summarized as follows:

- A NO_x fleet average of 4.8 g/bhp-hr begins in 2002 for both diesel and alternative fuel paths, which will require some transit agencies to retire their oldest, highest polluting buses.

- Ultra low sulfur diesel fuel (15 ppm wt.) is required beginning July 1, 2002.

- All pre-2004 diesel buses have to be retrofitted with ARB-certified, 85 percent efficient diesel particulate filters. The retrofit begins in 2003 and will be completed through 2007.

- New bus engines have to be certified to increasingly more stringent emission standards (Table 2-5).

- Ultimately, 15 percent of new purchases have to be zero emission buses, ZEB (Table 5).

The urban transit bus fleet rule requirements and emission standards are summarized in Table 2-5.

Table 2-5. California Urban Transit Bus Fleet Rule.

Date	Diesel Path		Alternative Fuel Path	
	NO_x, g/bhp·hr	PM, g/bhp·hr	NO_x, g/bhp·hr	PM, g/bhp·hr
2000	4.0	0.05	2.5*	0.05
7/2002	Ultra low sulfur diesel fuel		Ultra low sulfur diesel fuel	
10/2002	2.5 NO_x+NMHC	0.01	1.8 NO_x+NMHC*	0.03
10/2002	4.8 NO_x fleet average		4.8 NO_x fleet average	
2003-07	Diesel particulate filter retrofit		Diesel particulate filter retrofit	
7/2003	3 ZEBs for large fleets (>200)			
2004	0.5	0.01		
2007	0.2	0.01	0.2	0.01
2008	15% of ZEBs for large fleets (>200)			
2010			15% of ZEBs for large fleets (>200)	

Notes:
Shaded areas show existing requirements and existing optional emission standards
* - Optional standards. Although transit agencies on the alternative-fuel path are not required to purchase engines certified to these optional standards, it is expected that they will do so in order to qualify for incentive funding.

Model Year 2007 and Later[4]

On December 21, 2000 the EPA signed emission standards for model year 2007 and later heavy-duty highway engines. The rule includes two components: (1) emission standards, and (2) diesel fuel regulation.

The first component of the regulation introduces new, very stringent emission standards, as follows:

- PM - 0.01 g/bhp-hr

- NO_x - 0.20 g/bhp-hr

- NMHC - 0.14 g/bhp-hr

The PM emission standard will take full effect in the 2007 heavy-duty engine model year. The NO_x and NMHC standards will be phased in for diesel engines between 2007 and 2010. The phase-in would be on a percent-of-sales basis: 50 percent from 2007 to 2009 and 100 percent in 2010 (gasoline engines are subject to these standards based on a phase-in requiring 50 percent compliance in 2008 and 100 percent compliance in 2009).

Emission certification requirements also include the SET test, with limits equal to the FTP standards, and NTE limits of $1.5 \times$ FTP standards. Effective with the 2007 model year, the regulation also eliminates the earlier crankcase emission control exception for turbocharged heavy-duty diesel engines. Crankcase emissions from these engines are treated the same as (i.e., added to) other exhaust emissions. Manufacturers are expected to control crankcase emissions by routing them back to the engine intake, or to the exhaust stream upstream of the exhaust emission control devices. The diesel fuel regulation limits the sulfur content in on-highway diesel fuel to a maximum 15 ppm by weight, down from the previous 500 ppm. Refiners will be required to start producing the 15 ppm sulfur fuel beginning June 1, 2006. At the terminal level, highway diesel fuel sold as low sulfur fuel must meet the 15 ppm sulfur standard as of July 15, 2006. For retail stations and wholesale purchasers, highway diesel fuel sold as low sulfur fuel must meet the 15 ppm sulfur standard by September 1, 2006. Refiners can also take advantage of a temporary compliance option that will allow them to continue producing 500 ppm fuel in 20 percent of the volume of diesel fuel they produce until December 31, 2009. In addition, refiners can participate in an averaging, banking and trading program with other refiners in their geographic area.

Ultra low sulfur diesel fuel has been introduced as a "technology enabler" to pave the way for advanced, sulfur-sensitive exhaust emission control technologies, such as catalytic diesel particulate filters and NO_x catalysts, which will be necessary to meet the 2007/2010 emission standards. EPA estimates the cost of reducing the sulfur content of diesel fuel will result in a fuel price increase of approximately 4.5 to 5 cents per gallon. EPA also estimates that the new emission standards will cause an increase in vehicle costs from $1,200 to $1,900 (for comparison, new heavy-duty trucks typically cost up to $150,000 and buses up to $250,000).

2.6 EMISSION REDUCTION TECHNOLOGIES

General

Impressive advances were scored in diesel engine technology over the past two decades. Today's diesels are smokeless, and emit extremely low unburned hydrocarbon and carbon monoxide emissions. Their nitric oxides as well as particulate emissions are well within the regulated levels. In addition, modern diesels whether light-, medium-, or heavy-duty, have excellent performance and maintain their superior fuel economy attributes coupled with good durability and reliability.

Aware of the ever-increasing regulatory pressure, engine and original equipment manufacturers are searching for new technologies in their attempts to produce clean-burning engines while preserving their good attributes. As part of this effort, suppliers to the diesel engine industry are also contributing towards the same goal by ensuring that their products are designed to work in concert with the core engine components and curtail harmful emissions. Traditionally, most of the innovation concentrated on in-cylinder emission reduction technologies. However, it does appear that the industry is fast approaching the point of diminishing return from in-cylinder developments. Emphasis is now placed on other measures, some of which may still deal with in-cylinder emission reduction technologies. Major areas of interest include alternative fuels to those traditional blends used in diesel engines. For instance, in recent years we have witnessed renewed interest in emulsions involving water, methanol, as well as other additives with various claims of improved combustion, lower emissions, or even better fuel economy. Even though exhaust gas recirculation (EGR) is not a new technology for NO_x reduction in diesel engines, it has recently attracted attention because of its implementation in heavy-duty engines. Its impact on lube oil quality and life has raised concerns since it may directly affect the engine's durability. It has been documented, however, that EGR does increase carbonaceous particulate and may require additional emission controls in the exhaust system to avoid excessive particulate emission.

Another area of interest is that of post-combustion emission reduction devices, commonly known as aftertreatment systems. From the more conventional diesel oxidation catalysts and diesel particulate filters, post-combustion exhaust treatment has progressed into more novel systems such as lean NO_x adsorbers, lean NO_x catalysts, selective catalytic reduction with various reductants, and other combination systems that use an integrated approach in solving emission problems. For instance, selective catalytic reduction (SCR), used in the past to reduce NO_x from large industrial installations, is now being developed for heavy-duty on-highway diesel engines. Diesel particulate filters (DPF) that are known for their ability in reducing PM, have previously suffered from regeneration complications, lack of reliability, and durability problems. Now they are being included in plans for serial production. In their advanced development and planned production configurations, both technologies depend heavily on engine speed, load, exhaust temperature, and other characteristics. In fact, the move to integrate engine and post-combustion emission control devices (PC-ECD) into one overall emission control system is gaining popularity.

Against the advancement in diesel engine technology, there is an emerging interest in better understanding of some emission species and their potential impact on health. In particular,

diesel engines are singled out for their propensity to emit substantial particulate emissions. While prior investigations in their health effects may have failed to conclusively link them with adverse health effects, particulate emissions have long been suspect. Laboratory testing involving animal exposure attempted to show cause and effect by applying particulate-laden pastes on rats and inducing cancer. However, correlation of such testing and conclusions derived from its results included serious flaws. Earlier work pointed to heavier hydrocarbon compounds, including polycyclic nuclear aromatics, adsorbed on carbon particles that are inhaled into the lungs as causing adverse health effects. Recent work, however, points to the physical characteristic of these particles especially their size as the villain. Uncertainty regarding the specific mechanism responsible for the potential adverse effect begs for more research to accurately define the chemical and physical characteristic of particles produced in the process of combusting organic materials in diesel engines.

Smoke has been traditionally measured by opacimeters that were adequate for their intended purpose. Particulate emission, sampled and analyzed according to EPA's specifications as detailed in the Code of Federal Regulations Section 40, is currently evaluated predominantly through gravimetric means. This method involves capturing particulate on a filter material during the performance of a standardized emission test, a procedure that allows further analysis to determine particulate constituents. The two major constituents are insoluble matter, mostly carbonaceous particulate, and soluble organic matter that is mostly unburned oil. Beyond this subdivision, it is customary to analyze the particulate sample to determine its sulfate content. There was little else done to gather information regarding particle size, its shape, its size distribution, or chemical composition as a function of size. Interest in these topics gathered momentum given the technological advances in diesel engine design, especially in relation to modern post-combustion emission control devices, and their potential interaction with particles' chemical and physical characteristics.

2.7 TECHNOLOGY

A. Fuels

Several publications have reported correlation between some fuel properties and regulated diesel emissions. Drawing general conclusions is, however, difficult due to such factors as inter-correlation of different fuel properties, different engine technologies, or engine test cycles. In heavy-duty engines increasing cetane generally leads to lower HC, CO, and NO_x emissions, while reducing fuel density lowers NO_x and PM but increases HC and CO. Light-duty engines have a different response to fuel than heavy-duty engines. Sulfur increases PM in both classes of engines. Figure 2-4 illustrates the effect of diesel fuel sulfur on total particulate for two heavy-duty engine calibrations. Sulfur is also known to interfere with several diesel emission reduction strategies.

Historically, fuel properties have been continuously changing for various reasons, including crude oil prices, source of crude oil, crude oil quality, refinery technologies, relative demand for diesel and gasoline fuel, and changing engine technologies. In the recent years, environmental considerations and emission legislation have been increasingly more important in the formulation and properties of fuels. A number of research studies have been carried out

to investigate the influence of fuel properties on emissions. The most comprehensive programs include the European Programme on Emissions, Fuels and Engine Technologies (EPEFE)[5] and the American Auto/Oil Air Quality Improvement Research Program (AQIRP). [6]
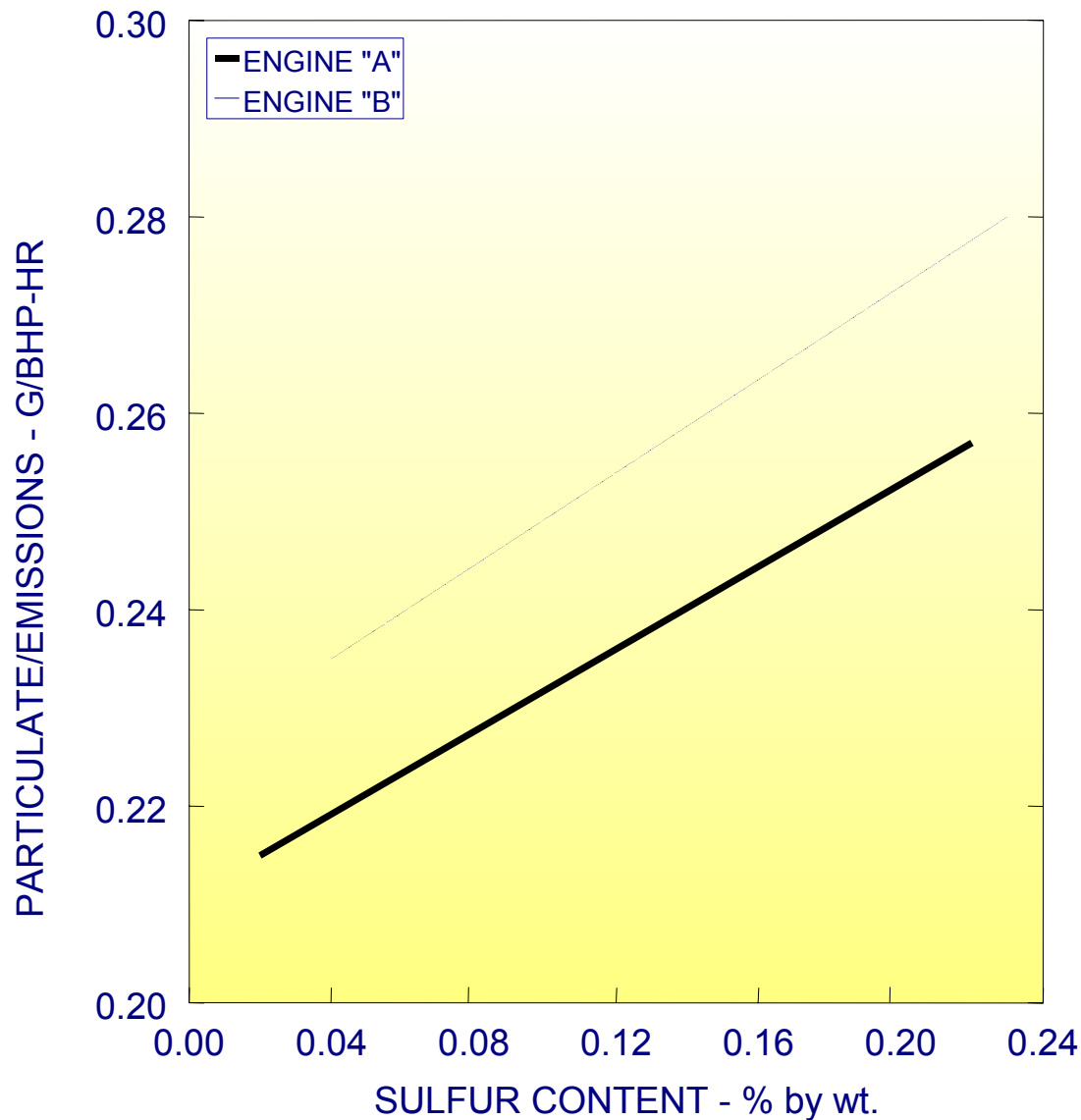
Figure 2-4. Effect of diesel fuel sulfur on total particulate emissions.

Despite the wealth of experimental data, the influence of some of the fuel properties on emission is still not clear. The following is a list of considerations that make the interpretation of results and the comparison of data from different studies difficult:

- Inter-correlation of fuel properties,

- Engine technologies,

- Emission test cycles,

- Aftertreatment technologies.

Inter-correlation of fuel properties. The properties of diesel fuel that influence emissions are usually intercorrelated. An example of this is density, aromatics content, and cetane number. Diesel fuels blending streams that contain high levels of aromatics are high in density and also have low cetane numbers.

Engine Technologies. Diesel engine technology has evolved in different directions around the world. In the 1990's, heavy-duty engines in the U.S. had large displacements and already featured a high degree of electronic control. In Europe the mechanical engine control still dominated. The engines were more highly rated and had smaller displacement. In Japan large displacement, naturally aspirated engines dominated the market. All of these different engine technologies tend to show somewhat different emission sensitivities to the fuel quality. It is also almost certain that the emission response of future engine technologies will be different from those currently in production.

The biggest difference in the fuel quality impact on emissions has been found between heavy-duty and light-duty engines. Apparently, the results from heavy-duty engine studies cannot be extrapolated to the light-duty engines, or vice versa, and the two engine classes should be discussed separately. Cetane number had more impact on older engines that had generally lower injection pressure. With modern injection systems came higher injection pressures coupled with smaller hole nozzles. This combination improved fuel spray atomization and shortened ignition delay mimicking the same effect of high cetane fuels. This feature and its effect is only one of many examples of engine design parameters that may dominate fuel effects.

Emission test cycles. Engines for different geographical markets are emission certified using different engine test cycles. Most research on the influence of fuel quality on emissions has focused either on U.S. technology engines tested on the U.S. transient FTP cycle or on European engines tested on the ECE R-49 cycle. The EPEFE study attempted to make a comparison between these two test cycles.[7] Considering the magnitude of effects found in the study and the spread of effects across the European fleet that was tested, the effects of fuel quality on emissions from the US and European sets of data are generally similar. Despite the different test cycles and different rates of pollutant formation, general extrapolation of fuel effects from one data set to another appears to be possible.

Aftertreatment technologies. Meeting future emission standards will require a more extensive use of exhaust gas aftertreatment technologies, such as diesel oxidation catalysts, lean NO_x catalysts, diesel particulate filters, or other techniques. The influence of fuel quality on these technologies is generally unknown. One exception is the fuel sulfur, which has been thoroughly tested for its influence on the performance of diesel catalysts. If an efficient aftertreatment device is used, it will become the primary driver on tailpipe emissions. From the emissions point of view the properties of fuel would have only secondary importance. Thus, the primary fuel issue would be its compatibility with particular aftertreatment technologies.

A1.   Fuel Effect – Heavy-Duty Engines

Important properties that influence emissions from heavy-duty diesel engines include the following:

- Sulfur content,
- Cetane number,
- Aromatics (total and polyaromatics),
- Density,
- Volatility (T90/T95),
- Oxygenates.

Sulfur

During combustion, the organic sulfur compounds in diesel fuel are first degraded to such molecules or radicals as H_2S, HS, S, or S_2 and then oxidized via SO radical to SO_2. The reactions are very fast, resulting in practically complete conversion of sulfur to SO_2. Volumetric concentrations of SO_2 in the exhaust gas can be easily calculated based on the mass balance of sulfur entering and exiting the combustion chamber. Other than the changes in the levels of exhaust SO_2, changing fuel sulfur content does not cause any observable effects on gaseous engine-out emissions. The emissions of HC, CO, and NO_x are practically independent from the fuel sulfur level. This can be illustrated by the data shown in Figure 2-5 obtained from the DOE-sponsored work (DECSE 2000a)[8], where emissions of CO were constant at all sulfur levels, HC increased slightly (3-8 percent) with increased sulfur level, and NO_x slightly decreased. Average fuel consumption (BSFC) increased with increased sulfur, but the data showed considerable scatter.
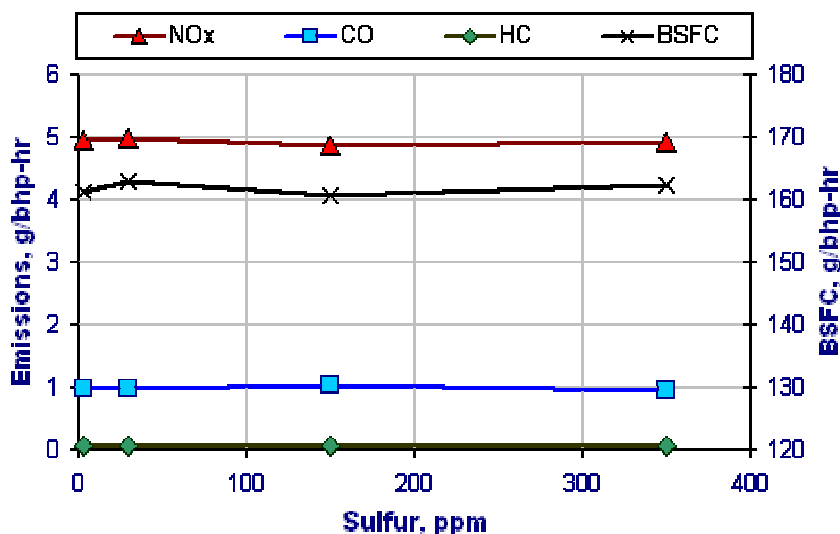
Figure 2-5. Fuel sulfur effects on gaseous emissions and BSFC[8].

Direct impact of fuel sulfur on emissions is limited to emissions of particulate matter (PM). A fraction of the fuel sulfur is converted to sulfur trioxide and sulfuric acid that, due to the

current definition of diesel particulate matter by regulatory authorities, is accounted for as PM emission. That emission is known as "sulfate particulates". Studies have shown that the amount of sulfur converted to sulfate is usually about 2 percent of the fuel sulfur content, and rarely exceeds 4 percent.[9] This conversion rate depends only slightly on the engine technology. It should be emphasized that the impact of sulfur is limited to sulfur particulates. There is no evidence that reduced sulfur levels have any influence on the carbonaceous portion of PM and on the black smoke.

Since sulfates are just one of several components of the PM emissions, lowering fuel sulfur levels has only limited potential as a means of PM control. The reduction of diesel fuel sulfur levels from 0.30 to 0.05 percent, as legislated in the U.S. in 1994, yielded relatively large benefits of about 0.04-0.08 g/bhp-hr PM reduction. However, further reductions of fuel sulfur from the current 0.05 percent to lower levels have only small incremental PM reduction benefit of about 0.008-0.016 g/bhp-hr.

An important aspect of the fuel sulfur levels is the compatibility of fuels with various emission control strategies. It has been shown that several aftertreatment technologies, including diesel oxidation catalyst, CRT^{TM} and catalyzed particulate filter, or NO_x adsorber/catalyst systems are sensitive to sulfur. Their performance is either impaired or totally blocked by sulfur compounds. Compatibility with exhaust aftertreatment, rather than a direct emission impact, is the prime driver in lowering the sulfur content in diesel to levels below 500 ppm.

Cetane Number

Cetane number influences the ignition delay in diesel engine. The cetane number is a measure of the fuels' ability to self ignite under compression. Increasing the cetane number reduces the ignition delay, as well as the size of premixed combustion. This feature results in lower NO_x formation rates due to a slower combustion pressure rise, which gives more time for cooling through heat transfer and dilution and leads to lower local gas temperatures. CO and HC emissions have been also reported to decrease with increasing cetane numbers. Both natural and additive improved cetane numbers appear to have the same emission benefit.

With the increasing requirements for lower NO_x, combustion events in new engines are being designed with little premixed burn. This is likely to challenge the traditional understanding of cetane impact on NO_x emissions. Indeed, for engines with little premixed combustion the impact of cetane number on NO_x is small or non-existent. Also the CO and HC emission benefits appear to be lower with new, low emission engines.

The effect of increasing cetane number on PM emissions is engine specific. In the majority of engines cetane number has no influence on PM emissions. In some engines a small but beneficial effect has been observed. In other engines increasing cetane numbers lead to increased PM emissions.[10]

Other effects of cetane number on the engine performance involve an increase in engine noise with lower cetane number. Some increase in fuel consumption with higher cetane number may also occur due to lower heating value of the higher cetane blends.

Aromatics

The effect of *total aromatics* on emissions has been much debated. Many studies in the past have failed to decouple the changes in aromatics from changes in density, T90, cetane, etc. They reported decreases in the HC and PM emissions with decreasing aromatics content which, apparently, were caused by changes in other fuel properties. More recent work that has separated the interactions of aromatic content with other fuel properties shows mixed results on the effects on HC, CO, and PM emissions. Most studies indicate no influence of the aromatics content on HC, CO, or PM.

Decreasing total aromatics from 30 to 10 percent does, however, produce a small benefit (0-5 percent) in NO_x emissions. This effect has been attributed to the high flame temperature associated with aromatic compounds. By reducing aromatics the flame temperature would drop leading to a lower NO_x production rate. Another possible mechanism is related to the high C/H ratios in aromatic compounds. High C/H leads to higher amount of CO_2 relative to H_2O during combustion. Since CO_2 has a higher tendency to dissociate at high temperatures, high aromatics fuels will produce higher concentrations of oxygen radicals, O·, which, in turn, will collide with nitrogen molecules yielding higher production rates of NO.

More recent studies have attempted to isolate the influence of *polyaromatics* or polycyclic (di- and tri-) aromatics from that of the total aromatics. Reducing polyaromatics appears to reduce HC and NO_x emissions but has no effect on CO emissions. It also shows a significant benefit for PM emissions in older high emitting engines (> 0.1 g/kWh). In modern low emitting engines reducing polyaromatics has little effect on PM emissions.

These effects of polyaromatics are attributed, like aromatics, to their high flame temperatures and high C/H ratios. The C/H ratios in polyaromatics are even higher than those in monoaromatics.

Density

Density is an important fuel property with respect to volumetric fuel economy and maximum power. In general, the energy per unit volume increases with increasing density. Studies that decouple the effects of density from those of other fuel properties (e.g. aromatics) prove that it is also an important factor influencing regulated diesel emissions.

It is critical that engine power output is maintained constant while assessing the influence of fuel density on emissions. If comparisons are made without adjusting to constant power output, then lower density fuels will produce lower maximum power and, thus, lower emissions. In such cases lower NO_x emissions are observed due to lower peak pressure and temperature, as well as lower PM emissions due to the overall leaning of the air/fuel mixture.

Reducing density from about 0.86 to 0.81 g/cm^3 has a beneficial effect on PM emissions. That effect can be as high as 20 percent in older more polluting engines (PM > 0.25 g/kWh), and becomes gradually lower as the engine-out particulate emission decreases. Modern engines (PM < 0.1 g/kWh) show very little or no change in PM emissions in response to changes in fuel density.

Reducing density also produces a small reduction in NO$_x$ but a large increase in HC emissions and a small increase in CO. The increase in HC is especially well pronounced in engines that are already high emitters (PM > 0.15 g/kWh).

The effect of density on emissions is related to complex physical interactions with the fuel injection system, which can lead to changes in the dynamic timing and mass injection flow rate. [7]

Volatility

The back-end volatility of diesel fuel, expressed as the 90 or 95% distillation recovery temperature (T90/T95), has some effect on emissions. When the volatility is reduced, a slight increase in HC and CO and a small decrease in the NO$_x$ emission is observed. There is no effect on PM emissions when the volatility is reduced. Given the small nature of these effects, diesel fuel volatility should be considered a minor factor in determining emission performance.

It should be expected that the volatility effect depend on the composition of the back-end. For example, heavy alkane waxes of high cetane numbers would give some emission benefit, compared to low cetane polyaromatics.

Oxygenates

There is an increasing interest in adding various oxygenates, such as biodiesel or alcohols, to the diesel fuel. That interest stems from the availability of oxygenates from biomass feedstocks. Emission benefits are sometimes claimed for such fuel blends. Once again, the majority of emission studies fail to decouple the addition of oxygenate from changes in other fuel parameters (e.g. density) that occur as the fuel is diluted by the oxygenate. In addition, blending oxygenate into the fuel reduces the fuel energy density and, thus, changes the emission levels. The engine must be recalibrated to its original power output before valid comparisons can be made. Therefore, the current oxygenate emission data should be considered tentative.

Studies on the emission influence of oxygenates seem to indicate some decrease of PM emissions, a slight decrease in CO, and an increase in HC when oxygenate content is increased from 0 to 4 percent.

Summary

With the exception of sulfur, fuel quality effects have much less significance in modern, clean diesel engines than they used to have in older, more polluting engines. Apparently, very little or no emission improvement can be achieved in modern, clean diesel engines by changing fuel quality. However, as new technologies are developed and incorporated into heavy-duty diesel engines, the fuel sensitivities may change and the above trends may need to be re-appraised.

A2.   Fuel Effect – Light-Duty Engines

The EPEFE program has been the most comprehensive study on the influence of fuel properties on the emissions from light-duty diesel engines. All test vehicles and engines were complying with the 1996 European emission standards (PM=0.08, HC+NO$_x$=0.7, CO=1.0 g/km). A matrix of 11 diesel fuels was covering the following changes in fuel properties:

- Cetane number: 50 - 58
- Density: 0.855 - 0.828 g/cm^3
- Polyaromatics: 8 - 1 % wt.
- T95: 370 - 325°C

The fuel quality effects on light- and heavy-duty diesel engines were quite different. This is illustrated in Figure 2-6, which compares the emission changes corresponding to a simultaneous change in fuel properties across the entire tested fuel matrix (i.e. as specified in the above list).[12] Only PM emissions changed in the same direction in response to the fuel change. Emissions of NO$_x$, HC, and CO changed in different directions. According to that data, fuel sensitivity of light-duty engines appears to be larger than that of the heavy-duty engines (with the exception of NO$_x$ emissions).
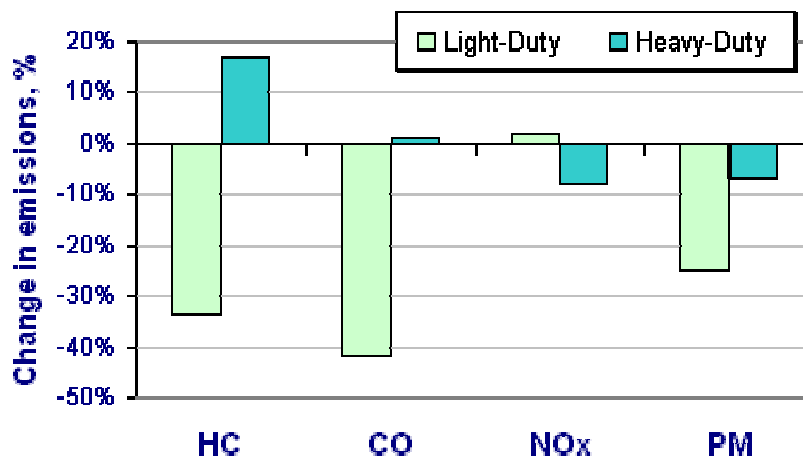
Figure 2-6. Fuel effects on light and heavy-duty engine emissions.

A3.   Water in Diesel Combustion

In general, adding water to the diesel combustion process decreases combustion temperatures and lowers NO$_x$ emissions. The most common methods of introducing water are direct injection into the cylinder, a process commercialized in certain marine and stationary diesel engines, and water-in-fuel emulsions. Emulsified fuels, due to increased mixing in the diesel diffusion flame, can be also effective in simultaneous reduction of PM and NO$_x$ emissions.

A3.1. Methods of Water Addition

Addition of water into the diesel combustion process is a known method to reduce NO$_x$ and, in some implementations, simultaneously reduce NO$_x$ and PM emissions. The very notion of introducing water into the cylinder of the diesel engine may sound controversial. After all, engineers have been taking great care to accomplish the exact opposite and protect the combustion chamber from water contamination, be it from the fuel or from water condensation in intake air coolers. The controversy around water addition is founded on the observation that water droplets impinging on the cylinder walls can immediately destroy the lubrication oil film.[13] This danger however, although very real, is posed exclusively by liquid water. Once water is evaporated, it can no longer affect the lube oil film. Thus, water addition methods that ensure that water droplets cannot contact the cylinder liner surface may be considered harmless. Further concerns have been raised that increased concentrations of water vapor in engine cylinder may result in condensation of water and/or sulfuric acid leading to corrosion problems. Apparently, these suspicions are not justified either, as the dew point of sulfuric acid at very high water/fuel ratios of 1:1 is increased by only up to 15°C.[14] Considering the temperatures in diesel combustion, condensation in the combustion chamber is not possible at any time.

In general, water can be introduced into the diesel combustion process using one of the following methods:

- Emulsified fuel
- In-cylinder water injection
- Water injection into the intake air

These methods are shown schematically in Figure 2-7.

Emulsion is a system consisting of two immiscible liquids, one of which is finely dispersed in the other. In all water/diesel fuel emulsions of practical importance water is dispersed in the form of fine droplets in the continuous diesel fuel phase. This type of emulsion, schematically shown in Figure 2-8, is often referred to as "water-in-fuel" emulsion. In the opposite configuration, with fuel dispersed in the continuous water phase, water would be much more likely to contact the cylinder liner surface and other metal parts, leading to corrosion and engine problems.
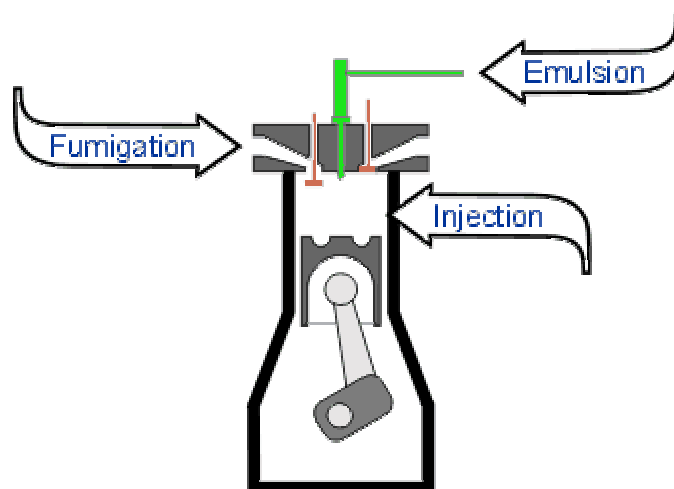
Figure 2-7. Water addition methods.
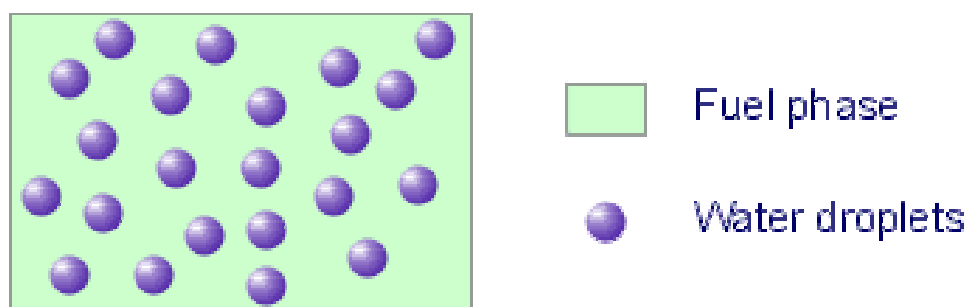
Figure 2-8. Water-in-fuel emulsion.

In practice, running an engine on water-fuel emulsion makes it possible to reduce NO_x by up to about 50 percent with the required water quantity being about one percent for each percentage point of NO_x reduction.[13] The limiting factor for water emulsions is the delivery capacity of the injection system. If emulsions are to be used without engine modifications (e.g., to substitute regular fuel in existing engines), the maximum quantity of water and the degree of NO_x reduction are both limited to some 10-20 percent. Even then, the engine may not be able to reach its rated power, running in effect at a slightly derated condition.

Emulsions are distinguished among other methods of water addition by the fact that water, being incorporated into the fuel spray droplets themselves, is introduced directly into the combustion flame area where emissions are formed. In addition to the NO_x benefit, which in all methods is attributed primarily to the lowering of combustion temperature by water, emulsions result in enhanced fuel spray atomization and mixing. Enhanced mixing which extends throughout the diffusion flame can bring quite impressive reductions of PM emissions. As a result, water-fuel emulsions are one of the rare diesel emission control strategies that can simultaneously reduce NO_x and particulate emissions without or with only a small fuel

economy penalty. Reduction of PM emissions by emulsions has not yet been as thoroughly researched as NO_x reduction. Nevertheless, as will be discussed later, the achievable effectiveness of PM reduction appears to be more than twice the level of NO_x reduction.

In-cylinder injection of water requires a separate, fully independent injection system, preferably under electronic control. This method offers the capability to inject very large quantities of water without the need to derate the engine. This system also allows switching the water injection on and off, as may be needed, without affecting engine reliability. Direct water injection needs to be carefully optimized with respect to injection timing, water consumption, emissions, and other parameters. This flexibility in optimizing parameters allows achieving NO_x reductions similar to those seen in emulsion systems, despite the fact that water is not introduced directly into the diesel flame area as an integral part of the spray. However, PM emission reductions, if any, do not match those with emulsified fuels. The complex development work required for water injection systems in different engine types makes this approach suited for OEM rather than for retrofit applications.

Fumigation, meaning the introduction of water into the intake air, is the simplest method of water addition. This method offers very little control over the injection parameters such as timing or spatial coordinates. For this reason, observed NO_x reductions tend to be lower than those with emulsions or direct injection. Fumigation typically reduces NO_x emissions by 10 percent for each 20 percent water addition to the fuel.[13]

If the fumigated water does not completely evaporate in the intake air, it will impinge on the cylinder walls causing disintegration of the lube oil film and engine damage. A safer approach is to fumigate water vapor rather than liquid. Water vapor may be generated using waste heat from the engine, such as from the exhaust gas and/or from the compressed charge air. Another possibility is to use steam, which may be available in certain stationary engine applications.

Regardless of the method of water addition, consideration must be given to the logistics of providing the water supply. The use of emulsifying agents allows for preparing emulsions that can remain stable for a number of days or even weeks. In this case, vehicles may be simply fueled with emulsion in place of regular fuel. Such application of emulsions is obviously limited to vehicle fleets that are centrally fueled from one facility where the emulsion would be prepared. Other water addition methods would require that water tanks and handling systems be installed on the vehicle. The obvious drawback of such systems is the large quantity of water that is needed for NO_x reduction, which would require large tanks and frequent replenishment. This is likely the main reason why water addition technologies attract more attention in stationary and marine applications, where supplying large quantities of water is less problematic. However, most systems for ocean going ships would work on fresh water only, thus requiring additional fresh water generation equipment.

A3.2. Impact on Combustion Process

Addition of water, often at large quantities, has a profound effect on the diesel combustion process. The occurring phenomena are not always clear and contradicting reports are easily found in the literature. Most likely, many of the water effects are engine specific, i.e.,

different magnitude or even direction in the change of a given parameter is observed in different engines. In general, the effects of water on combustion can be summarized as follows:

- Addition of water increases the mass of air-fuel mixture and the associated air quantity per same supplied energy and per unit time, resulting in improved atomization and mixing. The improved atomization effect is frequently attributed to droplet micro-explosions, especially in the case of fuel emulsion sprays,[15] but there is no universal agreement as to the effectiveness of this mechanism in the diesel engine.[16] The improved mixing is due to increased momentum of the vaporized fuel jet, which can entrain more air. Accelerated mixture formation and *increased ignition delay* are observed, leading to *increased premixed combustion*. This effect is consistently seen in all types of diesel engines.[17,18]

- The increased premixed flame causes higher maximum rate of heat release, higher rate of pressure rise, and higher maximum combustion pressure. Typical magnitudes of these phenomena are illustrated in the indicator diagram for regular fuel and water-fuel emulsion shown in Figure 2-9.[19]
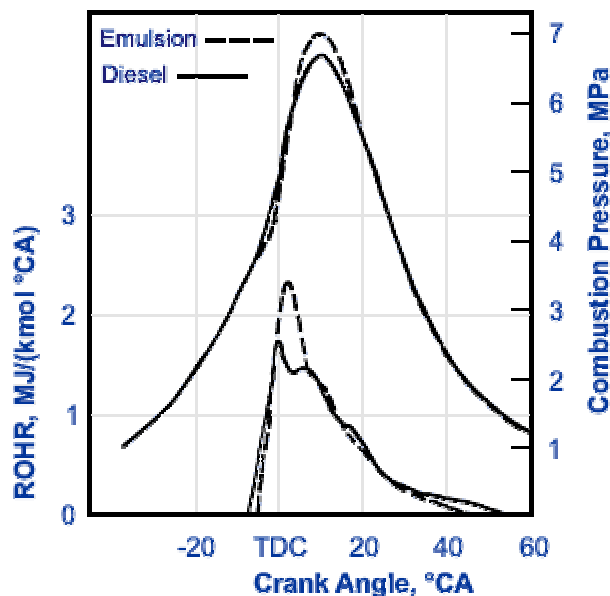
Figure 2-9. Influence of water on rate of heat release (ROHR) and combustion pressure. *(Single cylinder DI engine, injection timing 18.5° BTDC, BMEP = 0.52 MPa, nozzle opening pressure 19.6 MPa; water content 33.8%).*

- From the NO_x control perspective, the increased heat release rate and pressure are counterproductive effects. Water addition, however, also produces *reduced peak combustion temperatures*, the prime effect responsible for NO_x reduction in all methods of water addition.[16] Combustion temperatures are lowered thanks to the heat absorption effect due to an increase in both the gas mass and its specific heat[20] (remarkably, this effect bears a close similarity to the NO_x reduction mechanisms through EGR).

- Improved mixing and micro-explosion phenomena are responsible for *accelerated rate-controlled (diffusion) combustion*, resulting in a decrease in the total combustion duration. This assists in reducing NO_x formation from the diffusive flame.

- Chemical effects are also suspected, such as accelerated water gas reaction due to increased partial pressure of water. [20]

Some water addition systems, in particular those based on **emulsions**, as opposed to direct water injection or fumigation, have shown high reductions in PM emissions and smoke. This is usually explained by the increased mixing and increased local air excess ratio in the rate-controlled flame, leading to better oxidation of carbon, and by chemical effects which reduce formation of soot precursors in the premixed flame.[21] However, PM reduction mechanisms by water are generally less understood than those in NO_x reduction. A number of studies on water-fuel emulsion systems have measured increased PM emissions with increased water content.[22]

Very few studies focus on hydrocarbon and carbon monoxide emissions in water addition systems. The existing evidence indicates that HC emissions, both in the gas phase and as particulate SOF, are increased by water addition, sometimes as much as by a factor of 2 or even 3.[16] There is less consistency with CO emissions, with some studies measuring an increase, others a decrease in carbon monoxide. Evidently, many emissions depend on the particular engine and engine parameters. For example, a study in a DI engine showed that CO was reduced by emulsions at retarded injection timing, but unchanged or slightly increased at advanced injection.[19] Interestingly, the same tendency was found for smoke, which was most effectively reduced by emulsions at retarded injection timing. On the other hand, hydrocarbon emissions were increased by emulsions, especially at advanced injection timing.

Water addition is one of the few engine emission control strategies that allows for reducing NO_x (and, in some cases, PM) with little or no fuel economy penalty. Existing studies seem to be divided on the issue of engine thermal efficiency with water addition. Some authors measured a fuel economy penalty,[13] others a brake specific fuel consumption (BSFC) improvement,[19] still others no significant change. In the case of emulsions, it was shown that the BSFC may be improved by proper selection of the injection pump.[23] Theoretically, an improvement of engine efficiency with water addition seems to be inconsistent with the decreased combustion temperature effect. One study suggests the explanation, based on experiments with water injection into the pre-chamber on an IDI engine, that only localized peak temperature areas are quenched by water, while the mean combustion chamber temperature and, thus, the thermal efficiency and the BSFC remain practically unchanged.[18]

Fumigation of Water into Intake Air: Spraying of liquid water into the engine intake air is certainly the easiest to implement method of water addition. It was shown, however, that the associated NO_x reduction benefit is smaller than with the other methods.[13,23] In addition, water fumigation carries most risk, among all methods, of destroying engine lube oil film by water droplets that may reach, non-evaporated, the cylinder wall surface. For these reasons, injection of liquid water into the engine intake air stream attracts little attention today.

Corrosion problems may be minimized and possibly higher NO_x reductions may be achieved through fumigation of water vapor, in place of liquid water, into the charge air. It is generally

accepted that NOₓ emissions are reduced by simply increasing the humidity of the intake air. Increasing the absolute humidity of engine intake air by 0.01 kg/kg was reported to result in about 20 percent reduction in NOₓ, as illustrated in Figure 2-10.[20] This effect is roughly equivalent to using water-fuel emulsion of 20 percent water content.
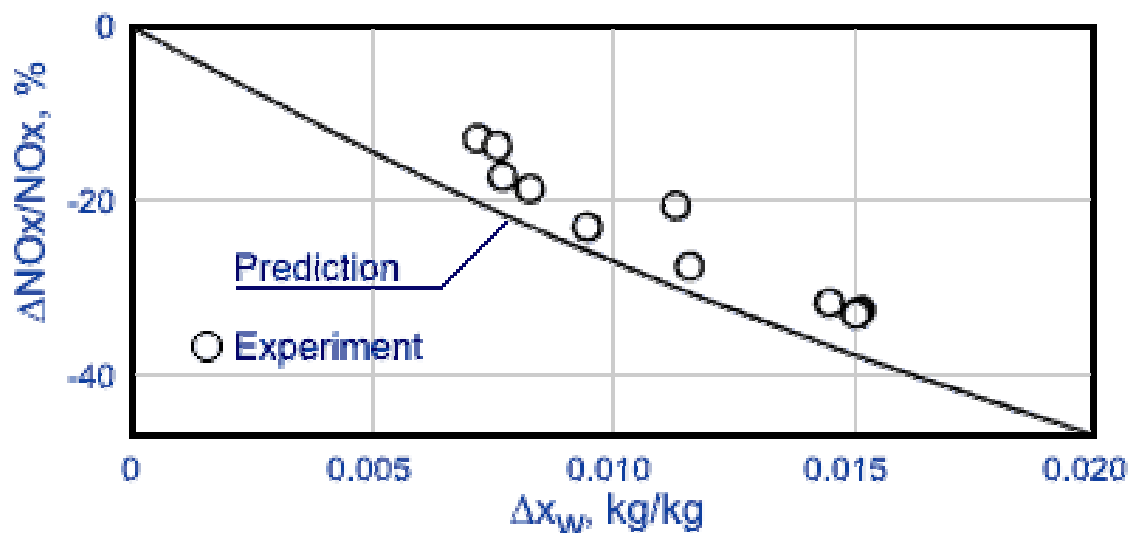
Figure 2-10. NOₓ reduction due to increasing absolute humidity.

The use of steam is most commonly researched in laboratories as the method of introducing water vapor into the intake air.[25] A potential drawback of steam systems may be increased PM emissions, which were reported to almost double at high engine loads.[26] Engine intake air may also be humidified by contact with hot water in a special humidification column. A system utilizing this principle that has been developed for ships will be described later in this report.

Direct Injection of Water: In this method, water is supplied directly into the combustion chamber through a dedicated nozzle. The water injection nozzle could be provided as a separate injector, or else may be a part of a tandem, water-fuel injector. In either case, the injection of water must be controlled independently from fuel injection in regards to timing, rate, and quantity. Very careful process optimization is required to ensure that water is supplied into the right area at the right time. To maximize NOₓ reduction, water must be supplied into the flame area at the time when emissions are formed. From the spray formation perspective, the best congruence of water and fuel sprays is achieved when both liquids are injected in parallel. Such parallel injection, however, may not optimally correspond to the period when most of the NOₓ is formed. For this reason, part of the water should be injected already at the beginning of combustion. Late injection of water is not only useless from the NOₓ control perspective, but was also reported to increase fuel consumption.[13]

The sensitivity of NOₓ reduction to the injection geometry and timing is illustrated in Figure 2-11,[18] where position A and B denote different configurations of the fuel and water injection nozzles. The optimization must also include other emissions, such as CO, HC, and

smoke/PM, which likewise depend on the water injection timing, but may not follow the NO_x reduction pattern.
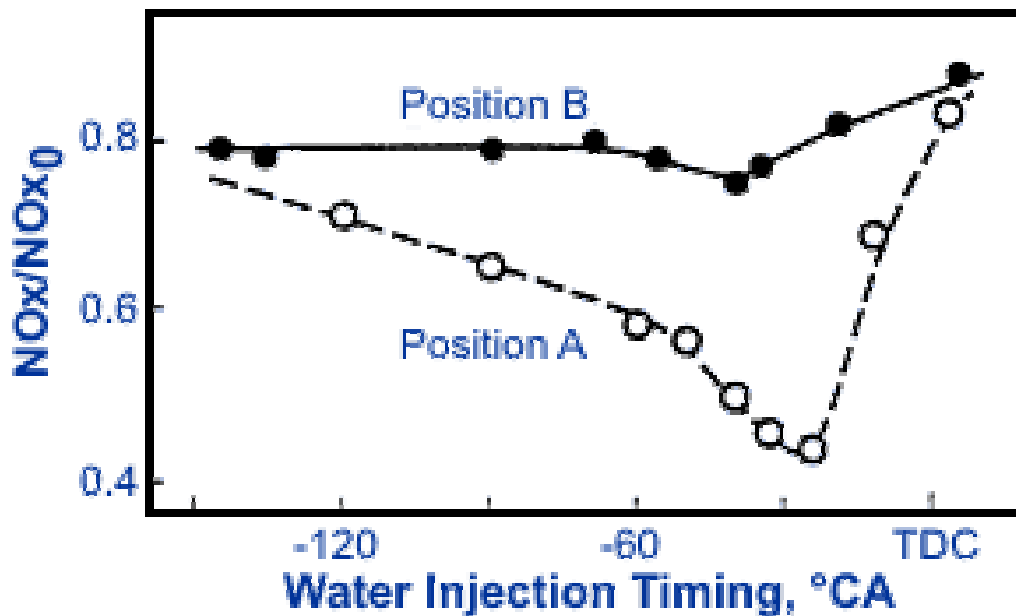
Figure 2-11. Effect of water injection timing and location on NO_x reduction.
(Water:fuel = 0.6; n=1500 rpm; brake mean effective pressure (BMEP) = 0.6 MPa; injection into the pre-chamber of IDI engine).

Direct water injection appears to be not very effective in controlling PM. Only slight reductions of PM emissions were measured in the above study. More sophisticated direct injection techniques, such as stratified water-fuel injection, have been proposed which may facilitate simultaneous NO_x and PM control in direct water injection systems.[27] Optimized direct water injection systems for NO_x control show water consumption levels that are comparable to those seen in emulsions. Figure 2-12 shows NO_x reduction at different water consumption (and, again, different nozzle configurations) as measured on a large, two-stroke marine diesel engine.[13] The fuel consumption was not referenced in the paper, but one can assume BSFC of 165-175 g/kWh as typical for this engine category. If so, the system shown in Figure 2-12 (arrangement 1) requires a water/fuel ratio of just below 1, or 50 percent water in the total water-fuel mix, to achieve approximately 50 percent NO_x reduction.
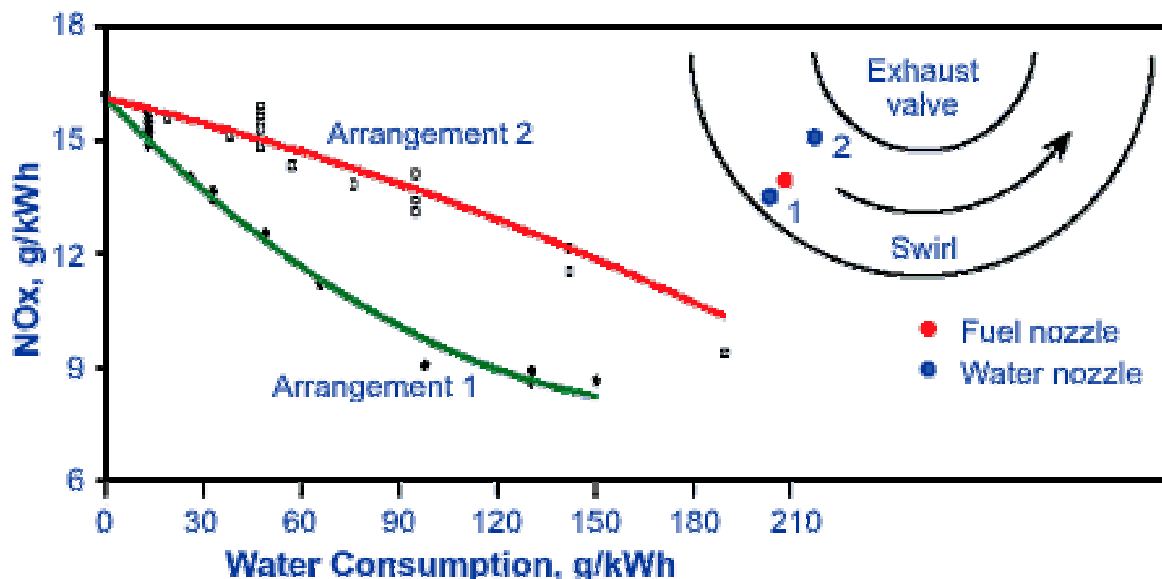
Figure 2-12. NO$_x$ reduction at different water consumption and injection nozzle arrangements.

A3.3. Fuel Emulsions

A3.3.1. Types of Emulsions

In emulsion systems, water is mixed with diesel fuel and the mixture is supplied through one injection nozzle. Depending on the method of mixing, either phase can be dispersed in the other. As mentioned before, in order to minimize water contact with internal engine surfaces, diesel fuel should form the continuous phase in which water should be dispersed in the form of small droplets. Water-in-fuel emulsions will also minimize the potential corrosion problems in the fuel system. Due to the differences in density and other physical properties, water-fuel emulsions are not stable. With time, the water droplets will coalesce, increasing their size, and settle down in the tank, forming pure water phase underneath the diesel fuel. In a NO$_x$ control system, the emulsion must have sufficient stability to pass through the injection process, i.e., the spray should be composed of fuel drops incorporating tiny droplets of water. This objective can be achieved using one of the following two approaches:

- Unstabilized emulsion - prepared on-vehicle, upstream of the injector,

- Stabilized emulsion - prepared off-board and then used for vehicle fueling.

Unstabilized emulsions separate quickly and must be prepared on-line in the engine fuel injection system immediately before the injection. This type of system involves two tanks, one for fuel, another for water, followed by two pumps and a mixing device. In one laboratory study, mixing was carried out as a two-stage process.[28] First, the liquids were mixed in a pre-mixer, where the internal phase (water) was injected through nozzles into the continuous phase (fuel) swirling through a cylindrical chamber. The mixture was then fed, through a gear pump, to an emulsifier. The emulsifier was a static mixing device featuring a system of nozzles and channels, where the blend drops dimensions were decreased due to jet diffraction,

impact, friction, and high pressure rates. The homogeneous emulsion was fed to the engine fuel injector.

The higher the densities difference between the two liquids in emulsion, the faster the separation. Therefore, more stable emulsions are possible with heavy fuels, such as those used in marine applications. Preparing unstabilized emulsions from lighter fuels, such as those used for highway vehicles, is more problematic. The use of unstabilized emulsions requires complex modifications to the engine and the injection system, which is an obvious drawback of this technique.

Stabilized emulsions involve mixing of fuel and water with the addition of small quantities (typically 1-3% of the fuel) of chemicals which facilitate the formation of emulsion (emulsifiers) and prevent or delay separation once the emulsion is prepared (stabilizers). The emulsion, prepared in an off-board mixing device, is used for fueling the vehicle, which in this case has only one tank and a single train fuel injection system. Emulsions must remain stable for a sufficient period of time to prevent separation in the fuel tank. In practical terms the required stability period must be at least several days, preferably several weeks.

If an engine designed for diesel fuel is to be fueled with emulsions, the injection system has to deliver more fluid. This can be achieved through increased injection duration, but the capacity of the injection system is often limited. The engine has to be either derated or the water content and the maximum achievable NO_x reduction must be limited to typically less than 20 percent. To obtain the maximum NO_x reduction also at full load, the injector nozzle may need to be changed to adjust for the longer injection duration, provided that fuel pump has sufficient capacity and the camshaft has sufficient strength.[23] With emulsions of high water content, redesign of the pump, the camshaft, camshaft drive, etc., may be also necessary. Once the injector design has been adapted to handle the increased quantity of injected liquid, the fuel consumption, as well as component temperatures, may be penalized when running without water.[13]

An important limitation on using emulsions is imposed by the maximum temperature in the fuel injection system. If the temperature exceeds the boiling point of water, the emulsion may be destroyed through the evaporation of water droplets. The effectiveness of the emulsifiers may be also compromised at high temperatures. In practice, emulsions can be used in engines equipped with pump-line-nozzle systems, but may not be suitable for common rail engines, where fuel temperature in the return lines may significantly exceed 100°C.

Low ambient temperatures may also limit the use of emulsions in cold climate areas, where freezing of the water portion may occur. The low temperature limit of emulsions may be extended through adding antifreeze agents (e.g., methanol) to the formulation.

A3.3.2.   Impact on Combustion and Engine Performance

Properties of emulsified fuels differ significantly from the properties of pure diesel fuel, resulting in numerous engine effects. Literature reports indicate that water droplets in the emulsion are relatively uniform and scattered within a range of 2 - 5 μm, with an average

diameter of around 1 μm. There is a tendency that the number of larger droplets increases with increased water content in the emulsion, as shown in Figure 2-13.[17]
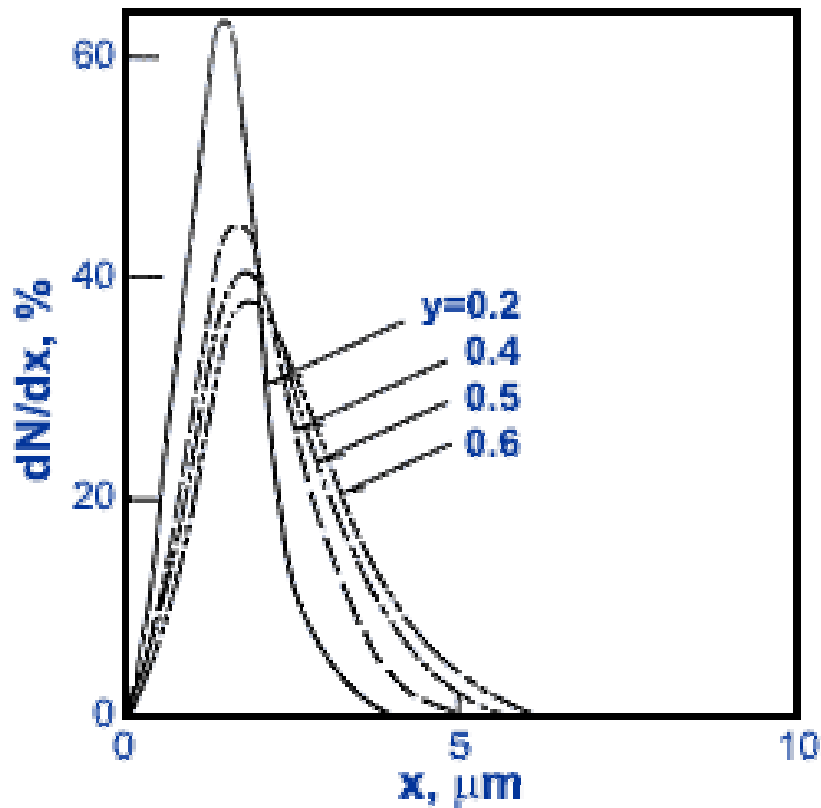
Figure 2-13. Effect of water fraction (y) on water droplet size distribution by number of particles (N) and by size (X). *(y - mass ratio of water to the total emulsion)*.

Fuel viscosity is an important variable affecting spray characteristics in diesel combustion. Water-fuel emulsions show increased viscosity with increasing water content. This, in turn, changes the size distribution of fuel droplets in the spray towards larger sizes, as shown in Figure 2-14.[17]

The density of emulsified fuel should in theory increase in proportion to the water content. Some published data indicates that emulsions may contain air bubbles, making their bulk density a little less than the sum of its fuel and water components. The air bubbles content was estimated to be between 1×10^{-4} and 2×10^{-4} of the water content.
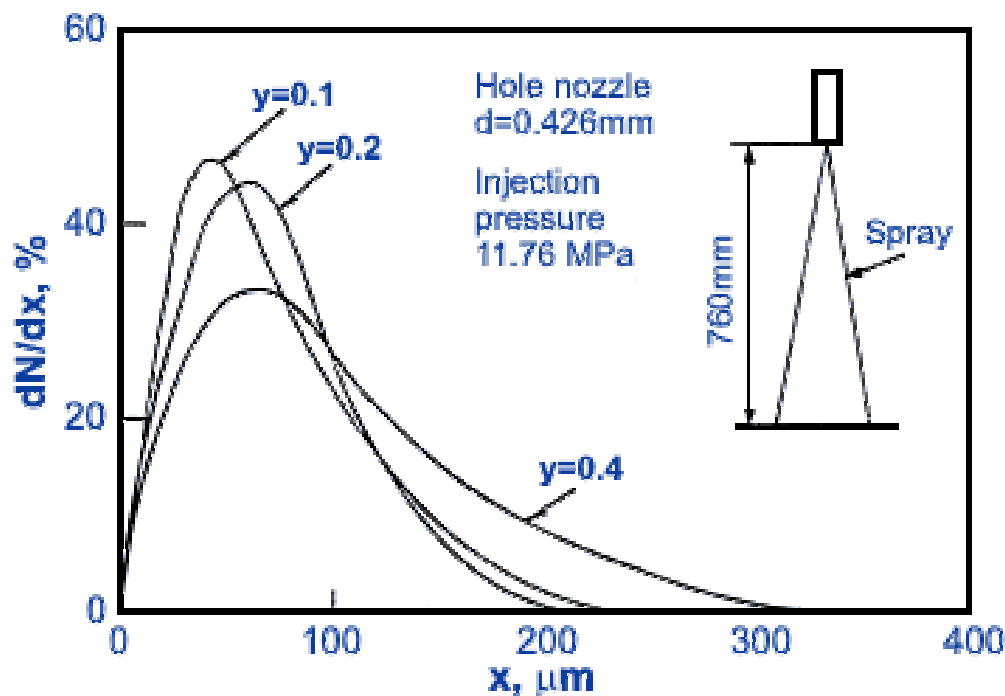
Figure 2-14. Effect of emulsified fuel on spray droplet distribution by number of particles (N) and by size (X). *(y - mass ratio of water to the total emulsion).*

Compared with pure diesel, emulsified fuels tend to increase the mean excess air ratio in the spray and its final penetration. Other spray characteristics such as spray angle and volume were reported to deteriorate.[19] Due to the higher amount of injected liquid and the changes in its properties, the injection rates are lower and the injection period is longer. Depending on the particular engine and injection system, the overall duration of combustion may be either shorter (due to the shortened rate-controlled flame) or longer. Some authors reported dramatic increases in the duration of combustion, as high as 10 degrees crank angle, as measured on large stationary engines with water addition of 30 percent.[23]

Rough, unstable engine operation during transients has been reported with emulsions.[17] The effect was explained by fluctuations in injection timing. The increased viscosity of the emulsified fuel was believed to decrease the leakage quantity at the injection pump, which advanced the start of fuel injection. On the other hand, the emulsion contained a certain quantity of air bubbles, which decreased its bulk density and the bulk modulus of elasticity, causing a delay in the opening of the injection nozzle. The relative magnitude of these effects changed following the random scatter of air bubbles and water droplets in the fuel, causing fluctuations in the start of injection. Water-fuel emulsions have been reported to increase engine noise levels, especially at low speeds in IDI engines and at advanced injection timings in DI engines.[19]

A3.3.3. Impact on Emissions

Before discussing the emission performance with water-fuel emulsions, a general comment should be made on comparing emissions from different fuels or fuel additives. As commonly

known, emissions change with engine operating conditions, in particular with engine load and speed. For comparing fuel effects, a test is done with a baseline fuel, followed by tests with fuels under study. However, the change of fuel properties is likely to have impact on the engine. Quite often after switching to a different fuel the engine delivers a different amount of power. Care must be taken that after the fuel change the engine is operated at the same conditions and, delivers the same mechanical work. Otherwise, the measured emissions could not be the basis for comparisons of emission effects of the tested fuels or additives; rather, they would reflect a combined effect of the fuel change and the change in engine operating point. In the case of engine dynamometer test cycles, the engine must be recalibrated with each fuel to deliver the same rated power in every test.

The same holds true for engines operated on emulsions; any valid emission comparison must be based on a common reference point. This can be illustrated by Figure 2-15, which shows measured levels of NO_x concentration reduction using water-fuel emulsions.[28] The lower line (higher NO_x reductions) was based on measurements where the total mass flow of emulsion was equal to the flow of diesel fuel in the baseline test. In the upper line measurements, the fuel portion of emulsion matched the fuel flow in the baseline test. Power delivered by the engine (assuming constant thermal efficiency) is proportional to the amount of diesel fuel that was consumed. Therefore, NO_x reductions shown by the lower line are in fact a combined effect of engine derating and emulsions. The upper, equal fuel energy line represents NOx reductions attributed to the effect of emulsion alone.
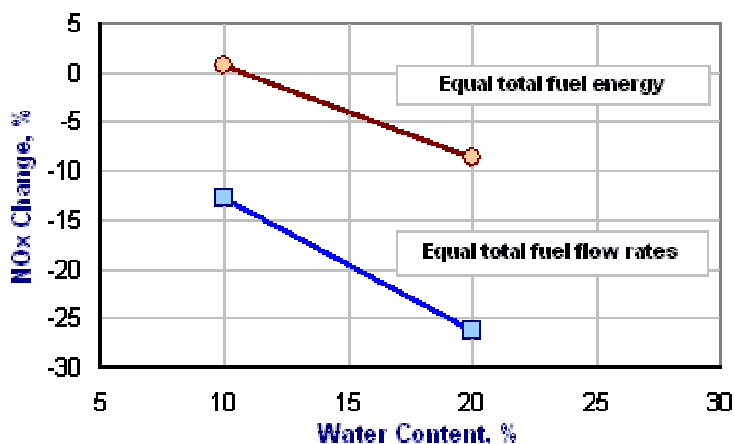
Figure 2-15. NO_x reduction for different fueling options.

Typical effect of water emulsions on NO_x is shown in Figure 2-16, which also illustrates the combined effect of retarded injection timing.[13] The measurements, both baseline and emulsified fuel, were taken at 75 percent of the nominal maximum load of the engine.
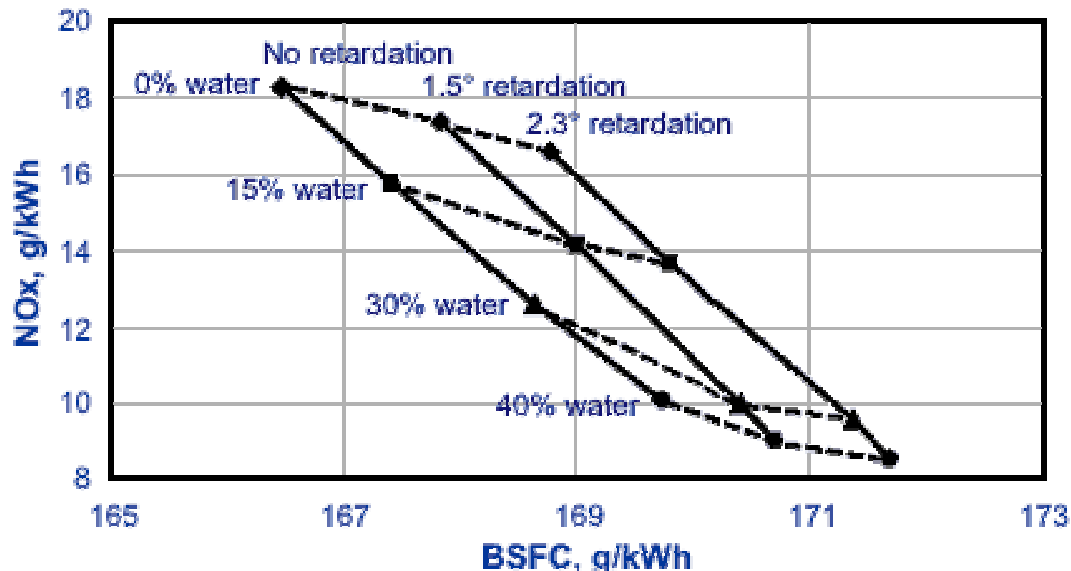
Figure 2-16. Influence of emulsion water content and injectiong timing on NO$_x$ emissions. (Sulzer 7RTA84T two-stroke engine, 75% load).

Solid lines in the graph refer to constant injection timing, while the dashed lines represent constant water content in the emulsion. s seen in the graph, increasing the water content in the fuel has an inversely proportional effect on NO$_x$ emission. Running the engine with 40 percent reduced NO$_x$ by about 45 percent. Some additional reduction is possible through the use of retarded injection. There is a small fuel economy deterioration with increased water content; at 40 percent water, the BSFC penalty amounts to about 1.2 percent. It is evident from the chart that, for the same NO$_x$ benefit, the use of retarded injection timing brings much higher BSFC penalty than the use of emulsion.

Injection timing appears to be an important variable, which can be used to optimize the effectiveness of emulsions. In tests on a Caterpillar 3406B marine diesel engine, a 20 percent water emulsion had practically no NO$_x$ effect at injection timing of 30°BTDC, but was very effective at 17° before top dead center (BTDC).[21] The effect of emulsion on reducing PM emissions was also higher at the retarded injection timing.

Water-fuel emulsions may be also an effective means of controlling diesel particulates. There are many reports, both from the older literature [16] and from newer experimental studies[21], showing very high PM reductions. The apparent percentage PM reductions in emulsion systems are much higher than the simultaneous NO$_x$ reductions, perhaps by a factor of 2. The published data, however, shows such degree of scatter that we are in no position to make generalizations. Reports vary from some 20 percent PM emission reduction at 40 percent water to 70 percent PM reduction at 10 percent water. Some authors compare emulsion test results from derated engines with baseline data at full ratings; such reports have a limited or no reference value. The PM performance of emulsions is also obscured by the differences in sulfur levels between studies and the unknown contribution of sulfates.

To make the PM effect even more confusing, some studies measured increased PM levels with emulsified fuels. Total particulates increased with added water in a study on a MAN 10L67GBE-S, 16,255 kW @ 125 rpm, two-stroke diesel engine.[23] Lower PM increases were measured with a larger injection pump, which is an indication that PM reduction may be sensitive to the type of engine and injection system. Large increases in the total combustion period, which were measured in the above study, may be also related to the increased PM, as the PM reduction effect is related to improved mixing and shorter diffusion flame period with emulsions. An increase of PM with emulsions appears to be also more likely in large, two-stroke, stationary engines, while more reports on decreased PM come form smaller, four-stroke engines.

Emulsions were reported to be compatible with diesel oxidation catalysts, which can bring an additional PM reduction benefit through the oxidation of the soluble organic fraction (SOF).[21] Catalysts may be especially beneficial in emulsion systems that increase the SOF fraction of diesel particulates or gaseous emissions such as HC and/or CO.

A3.3.4. Practical Embodiments

High quantities of water that are required to achieve any significant NO_x reduction are a major drawback of all water addition methods. It is especially true in highway applications, where re-filling of high volume water tanks or using high water content emulsions is not practical. More commercial interest in water addition methods has been observed in the stationary and marine engine markets. The accumulated experience indicates that water addition can be a viable NO_x emission control strategy. In particular, water addition systems can be designed to operate with little or no fuel economy penalty and without causing adverse engine effects, as demonstrated in a number of large engine installations. In one such application, a 20 MW diesel powerplant had been operated for over 10 years on fuel of 30 percent water content with no technical problems.[23] A number of water addition systems for large marine engines were under development in the late 1990's, in anticipation of the international IMO MARPOL NO_x emission limits for ocean going ships.

More recently, commercial water-fuel emulsions have been developed for mobile applications. Without engine modification the maximum water content is limited by the capability of injection system, setting a practical limit on the maximum NO_x reduction of about 20 percent. However, a simultaneous relatively high PM emission reduction may enable commercialization of emulsions in certain mobile engine applications.

The following are descriptions of three commercial water addition systems. These example products were selected to illustrate commercial implementations of all of the three different water addition methods: emulsion, direct injection, and fumigation.

A4. Commercial Status

A4.1. PuriNOx Emulsion

The Lubrizol Corporation, a manufacturer of lubrication oil additives and related chemicals, has developed a water-emulsion system being commercialized under the trade name "PuriNOx". The PuriNOx fuel involves mixing of diesel fuel and water with emulsifying and stabilizing additives made by Lubrizol. It is designed for direct injection heavy-duty diesel engines in centrally-fueled fleets.

A special PuriNOx blending unit is approximately the size of a shipboard container: 6 m wide, 2.4 m deep and tall. It becomes functional with electrical supply and diesel fuel and water line connections. The capacity of the blending unit is 20 million liter of emulsified fuel per year. The blending unit can be installed by an operator of a centrally fueled fleet of diesel vehicles such as an urban bus garage. The PuriNOx blend can be used to fuel existing vehicles without the need for engine modification.

PuriNOx fuel includes 20 percent water blended with 77 percent diesel fuel and 3 percent additive package (additive 1121A). To enable the use of water blends at low ambient temperatures, winter PuriNOx fuel incorporates methanol. A winter formulation was developed consisting of 16.8 percent water and 5.7 percent methanol, blended with 74 percent diesel fuel and 3.5 percent winter additive package.[29] The water content may be limited at levels of less than 20 percent by regulatory fuel specifications. For example, PuriNOx formulations sold in the UK and Italy contain only 12 percent water, resulting in lower emission reductions than the 20 percent blend. PuriNOx blends have opaque, white appearance, resembling milk. Water droplet size in PuriNOx is below 1 μm. The emulsion has a good stability and can be stored in a tank without agitation for up to three months without water separation. Engines fueled with the emulsion experience approximately 15 percent power loss.

According to the manufacturer, PuriNOx fuel can offer NO_x reduction of up to 30 percent and PM emission reduction of up to 50 percent.[30] Emission reductions appear to be highly dependent on the engine type. PuriNOx has been verified by the California Air Resources Board to provide emission reductions of 14 percent for NO_x and 62.9 percent for PM.[31]

The PuriNOx emulsion is compatible with catalysts. A combination of the emulsion with a diesel oxidation catalyst was reported to reduce PM emissions by 70 percent. The manufacturer has been also investigating optimization of emission reduction by combining PuriNOx with retarded injection and catalysts, concluding that both NO_x and PM were controlled more effectively at retarded injection timing.

A4.2. Wartsila Water Injection System

Wartsila, a Finland-based manufacturer of marine diesel engines, has developed a direct water injection system for large, ocean going vessels.[32] First systems were installed on ships around 1999. The system is commercially available for new Wartsila engines, or as retrofit equipment for existing engines.

The Wartsila system reduces NO$_x$ emissions by 50 – 60 percent (down to typically 4-6 g/kWh on marine diesel oil and 5-7 g/kWh on heavy diesel oil) operating at an injected water to fuel ratio of 0.4 - 0.7 (which corresponds to 28 – 41 percent water in the water-fuel mix). NO$_x$ reductions are most efficient at engine loads of 40 percent and above. The engine can be operated in "no-water" mode if desired. It can be switched to the "no-water" mode at any engine load. In alarm situations, the switch to "no-water" mode is automatic.

Main components of the Wartsila system are shown in Figure 2-17. Filtered, clean water is fed to the engine by two water pressure units, each of the size 1 m $\times$ 1 m $\times$ 1.7 m. The first low pressure unit supplies 0.35 MPa water pressure to the second, high pressure unit, which in turn supplies 20 - 40 MPa water pressure to the combined fuel water injectors in each cylinder. A "water fuse", a safety device shutting off the flow of water into the cylinder in case the water needle becomes stuck, is installed in the water line at each cylinder. The entire system is electronically controlled, with water injection timing advanced relative to the fuel timing. A small fuel economy penalty is associated with the water process and the parasitic load from the water pumps.

Figure 2-17. Components of the Wartsila Direct Water Injection system.

An important component in the system is the dual-fluid injector, which allows for simultaneous delivery of water and fuel into the cylinder. The injection of each fluid is controlled separately through dedicated solenoid valves. Fuel and water enter the cylinder through a dual nozzle with two separate needles, Figure 2-18.

Figure 2-18. Combined nozzle for injecting fuel and water in large two-stroke diesel engine.

A4.3. Pielstick Humid Air Motor

The Humid Air Motor (HAM) is a water vapor fumigation system developed for ocean ships by the French engine manufacturer Pielstick.[33] It is now offered as an option available for a number of four-stroke marine Pielstick engines. The HAM system can achieve up to 70 percent NO_x reduction with no increase in smoke or HC emissions. In this system engine charge air is humidified using hot water. The HAM humidification tower can replace the engine intercooler, or other waste heat sources can be used, such as jacket cooling or exhaust gas heat. In the configuration shown in Figure 2-19, both the exhaust gas and the charge air heat are used in the HAM humidifier.

Water in the HAM process is completely evaporated, preventing entraining water droplets into the cylinder. The system has been designed to tolerate low quality water, including sea water. Thanks to the evaporation process, there is no induction of impurities from water into the engine cylinder. The HAM system is started simultaneously with the engine, but stopped 15 minutes before the engine shuts down, to allow for drying of the system.
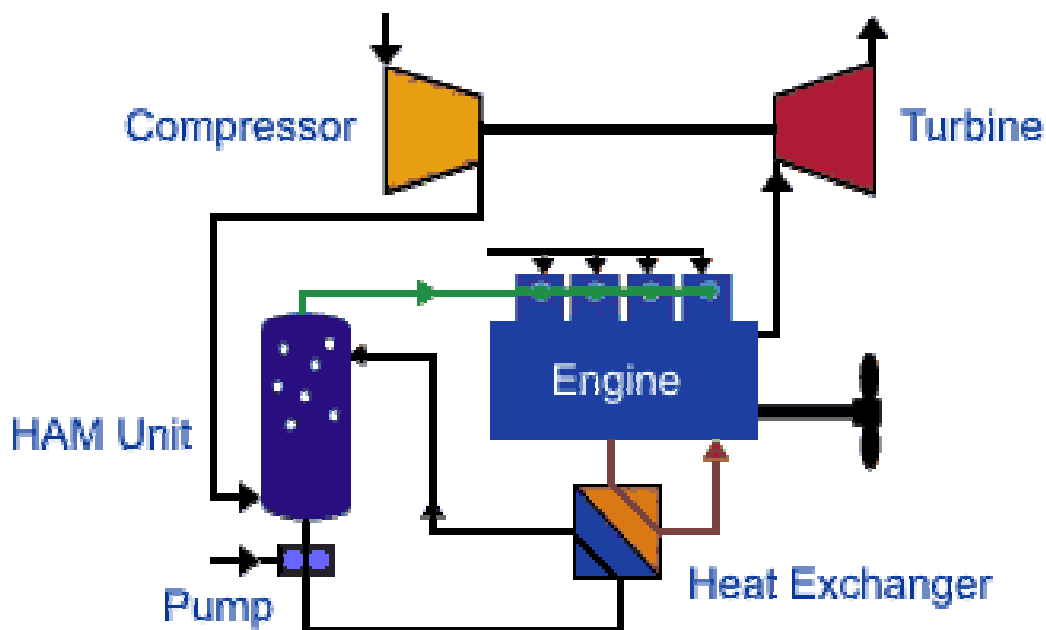
Figure 2-19. Schematic representation of the Pielstick Ham system.

A5.   Clean Diesel Fuels

Diesel fuels and other petroleum products are traditionally manufactured by refining of crude oil. However, they can be also produced synthetically from various carbon bearing feedstocks. The feedstock that attracts the most attention today is natural gas. Worldwide reserves of natural gas are estimated at 140,000 billion cubic meters (bcm),[34] while annual global consumption is only 2,100 bcm. There are many remote ("stranded") natural gas reserves around the world that for various reasons are not readily accessible by pipelines. In several other locations natural gas that accompanies crude oil ("associated gas"), but is not utilized, is flared in huge quantities. Last, but not least, producing high quality liquid fuels from natural gas is an alternative to all other methods of gas utilization. Since liquid fuels are several times less expensive to transport than gas, conversion to liquids provides an opportunity to expand the use of natural gas while lowering the transportation costs.

The first, and perhaps the best known synthetic fuel technology is the Fischer-Tropsch (FT) process, which was developed in the 1920's in Germany. Commercial use of FT fuels, besides the two historical incidents of the World War II Germany and the South Africa during economic embargo periods, has been extremely limited. Nevertheless, the FT research work has been continued by several companies, leading to the development of a mature technological process of improving economy. Today, the major FT technology players include large oil companies, such as ExxonMobil, Shell, and Sasol. Research is also sponsored by governments, which perceive synthetic fuels as an important option for future alternative fuels.[35] Furthermore, small development-stage companies exist (e.g., Syntroleum or Rentech) that develop and license FT processes to others.

Because of the natural gas focus, synthetic fuel processes are frequently referred to as gas-to-liquid, or GTL, technologies. That term is not covering all synthetic fuel technologies, as

liquid fuels may be produced, and have been produced, from almost any carbonaceous feedstock that is either gaseous, liquid, or solid. Coal is a good example of a solid feedstock that was used for manufacturing of FT diesel fuel in the past. On the other hand, the term GTL is sometimes also used in relation to non-FT fuels, for example dimethyl ether (DME), which can be produced from natural gas feedstock as well. This report is limited to fuels produced through the Fischer-Tropsch synthesis, with focus on natural gas a the most important feedstock.

There are several reasons for the importance and attractiveness of synthetic diesel fuels:

-Synthetic fuels are compatible with existing engines, there is no need for engine modifications.

-Synthetic fuels are compatible with conventional diesel (comparable energy density, can be mixed with petroleum diesel, can be transported as liquid in existing petroleum infrastructure).

-The fuels can be designed to have very good properties for both engine performance and emissions.

-Synthetic fuels can be used neat or as a valuable blending stock, to improve the properties of petroleum fuels.

-The sulfur content is practically zero, making synthetic fuels compatible with a range of sulfur-sensitive exhaust gas aftertreatment technologies, such as NO_x adsorbers or the continuously-regenerated traps (CRT) or filters.

On the other hand, environmental concerns may present an obstacle in the commercialization of synthetic fuels. FT fuels manufactured from natural gas bring no discernible greenhouse gas benefit relative to petroleum diesel (unless the feedstock gas was flared before the production started). Only FT fuels made from biomass can provide a life cycle CO_2 emission benefit.

Potential locations for commercialization of GTL plants are in regions with ample low-cost gas resources, such as the Middle East, West Africa, and the North Slope in Alaska. Fields like those on Alaska's North Slope contain plenty of natural gas but are far from market. The Trans-Alaska Pipeline System offers the opportunity to transport GTL products through the existing pipeline and provide high-quality synthetic hydrocarbons to world markets. GTL technology could be important in locations where associated gas is re-injected or flared for lack of nearby markets. In these locations GTL plants could produce hydrocarbons that could be conveniently refined or, if upgraded, shipped directly to market in conventional tankers. Integration of GTL technology with production and other operations offers additional incentives. Use of the byproducts of the GTL process, such as steam, power, and nitrogen, can further enhance its overall commercial value. On the other hand, GTL fuels produced from pipeline supplied natural gas would not be competitive due the higher feedstock cost.

Process economy, as influenced by the high capital costs of FT processes and the market risks due to the fluctuation of crude oil prices, presents the main barrier for wider

commercialization of synthetic fuels. Whenever crude oil prices decline, economic challenges increase for synthetic fuels. The sensitivity of FT fuel cost to the crude oil price is illustrated in Table 2-6.[35] It is generally agreed that FT production is feasible only at very low gas prices on the order of $0.50/MMBTU (1 MMBTU = 1 million BTU = 1055 MJ), unless a premium is paid for environmentally friendly fuel.[36] It is also estimated that crude oil prices must be above $20 - $25 per barrel for FT plants to be profitable.

Table 2-6. Unit cost production of GTL Fuel, $/Barrel.

Cost Component	Refinery	GTL
Natural Gas (@$0.50/MMBtu)		$4.00
+ Crude Oil (@$17/Bbl)	$17.00	
+ Operating Costs	2.50	3.00
Total Cash Costs	19.50	7.00
+ Capital Recovery, Taxes	6.50	12.00
Total Cost to Produce	$26.00	$19.00

An important economic benchmark for comparing FT technology is the capital cost of building a manufacturing plant. For a refinery, that cost is in a range of $12,000 to $14,000 per daily barrel, while the cost of the various existing FT technologies is in a $20,000 to $30,000 per daily barrel range.[37] All of the above figures reflect the cost situation in the 1990's. Advances in technology continue to drive down the cost of manufacturing high-quality liquid products from natural gas. As shown in Figure 2-20, costs have been reduced over 50 percent since 1990 as a result of advancements in slurry hydrocarbon synthesis (HCS), improved syngas generation options, and new technologies for upgrading HCS products.[38]

Other, non-Fischer-Tropsch technologies that aim at producing less expensive synthetic fuels are also being researched. One of such ventures, involving Catalytica and Syntroleum, is developing a new class of catalysts for a direct oxidation of methane into methanol and liquid hydrocarbons.

Direct liquefaction of coal is another method that can be used to produce petroleum products (the FT synthesis using coal is also called the "indirect liquefaction of coal"). In this process, coal is converted to liquid hydrocarbons in a single step operation. Hydrogen is added to the coal during the conversion process to upgrade the liquid products, giving them characteristics comparable to petroleum. Research continues to improve the process economy.
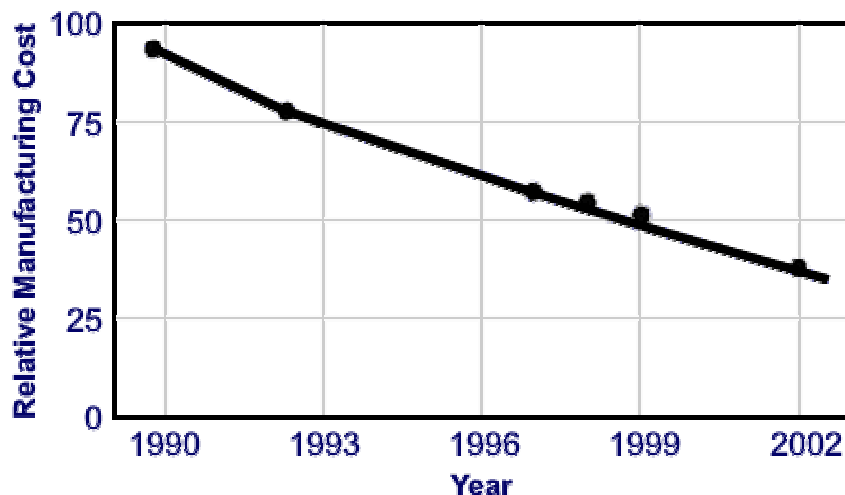
Figure 2-20. GtI process relative manufacturing cost.

A5.1. Properties of FT Fuels

Since a number of FT catalyst and reactor technologies exist, the properties of FT diesel fuels are likely to vary. The FT fuel properties can be also designed to suit a particular application by selecting the production process parameters. In general, in comparison to petrodiesel, synthetic fuels have the following qualities:

- Very good ignition characteristics, cetane numbers may reach 75 and higher,

- No (or very low) sulfur,

- Very low aromatics and polyaromatics content,

- Colorless and almost odorless appearance,

- Energy density similar to petrodiesel.

On the negative side, FT fuels are usually distinguished by:

- Poor lubricity, and
- Poor cold flow properties.

A very important feature of synthetic fuels is their compatibility with existing diesel engines. The only adjustment that may be required is increasing the lubricity of fuel in order to prevent excessive wear of the fuel injection system. That can be achieved using commercial lubricity additives. Doping the FT fuel with biodiesel, which has excellent lubricity properties, is also possible. Table 2-7 lists an example analysis of 100 percent Shell FT diesel fuel without and with a lubricity additive. The analysis is compared with fuel quality requirements from engine manufacturers, according to Caterpillar specifications.

A5.2. Emissions with Synthetic Fuel

A5.2.1.   Regulated Air Pollutants

A number of experimental studies showed emission benefits when comparing FT diesel fuels (neat or blends) with petrodiesel.[39] These findings are in agreement with the known fuel effects on emissions. High cetane number, low aromatics, and low sulfur—the basic properties of FT fuels—favor reductions in the emissions of several diesel exhaust pollutants in both heavy- and light-duty engines.

Various studies evaluate different FT fuels, which are manufactured by different processes and characterized by different properties. Therefore, exact comparison of the results is usually not possible. In some studies differences in the engine power output are observed, due to differences in the energy density of the tested FT fuel and petrodiesel. If the engine is not recalibrated to its original power rating, the validity of such emission comparisons may be limited. The emission effects of FT fuels, just as it is the case with other diesel fuels, tend to be engine specific. A general trend appears to be that older technology engines can achieve more emission benefit using better fuels than new engines of optimized combustion system. It should be realized that fuels, including the FT diesel, have only a secondary impact on emissions; the primary diesel emission drivers are combustion system and, if present, exhaust gas aftertreatment.

The potential emission impact of FT fuel and its blends in heavy-duty engines can be illustrated by the results of a Sasol fuel study, conducted on a 1991 DDC Series 60, 12.7 liter diesel engine.[40] The engine was tested on the FTP Transient test cycle. The FT fuel was blended with conventional U.S. No.2 grade diesel fuel. Emissions with the bends were compared with the emissions using No.2 diesel fuel and with California diesel fuel. Substantial emission reductions were achieved with the FT fuel, as presented in Figure 2-21 and Figure 2-22. It was found that blends of the FT and No.2 petroleum fuels in 40:60 proportion produced emissions equivalent to those with California fuel.

Table 2-7. Analysis of Shell Fischer-Tropsch (FT) Diesel Fuel.

Property	ASTM Method	100% FT Diesel	FT Diesel with Lubricity Additive	Fuel Requirements from Engine Manufacturer
Flash Point, °C	D93	72		legal limit
Cloud Point, °C	D2500	3		max not above the lowest ambient temperature
Water & Sediment, wt%	D1796	<0.02		0.1 max
Carbon Residue, wt%	D524	0.02		1.05 max
Ash, wt%	D482	<0.001		0.02 max
Distillation, °C T10 T90	D86	260 331		282 max 360 max
Kinematic Viscosity, cSt@40°C	D445	3.57	3.57	1.4 min, 20 max
Sulfur	D5453	<5 ppm*		3 wt% max
Corrosion, 50°C/3hrs	D130	1A		no.3 max
Cetane number	D613	>74**		40 min
Density@15°C	D4052	0.7845		
API Gravity@15°C, °API	D287	54		30 min, 45 max
Pour point, °C	D97	0		6° min below ambient temperature
SFC Aromatics, wt% Mono- Di- Poly-	D5186	0.1 0.1 0.1		
FIA, vol% Aromatics Olefins Saturate	D1319	0.1 0.1 99.8		35 max
Gum Content, mg/100ml	D381	0.2		10 max
Lubricity SLBOCLE, g	D6078	1700	4050	3100 min
Lubricity HFRR, µm	D6079	420/540/570	210	380 max
Carbon/Hydrogen, wt% Carbon Hydrogen Nitrogen Residual Oxygen (by diff.)	D5291	84.91 14.97 0.67 -1.09 Negligible		
Heat of combustion, Btu/gal Gross Net	D240	132,600 123,600		

* - below minimum measurement capability

** - above maximum measurement capability
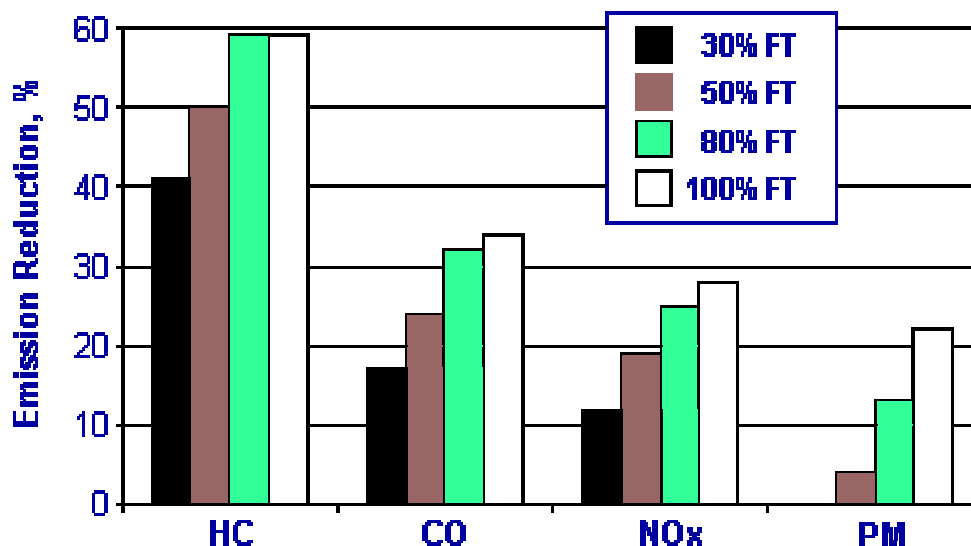
Figure 2-21. Emission reduction using Fischer-Tropsch (FT) fuel compared to No. 2 diesel fuel.
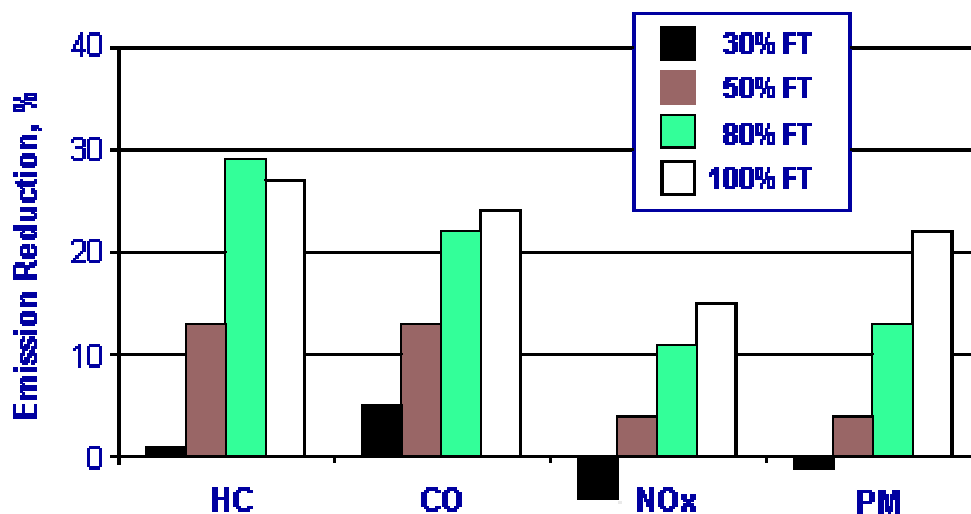
Figure 2-22. Emission reduction using Fischer-Tropsch (FT) fuel compared to California diesel fuel.

A second stage of the Sasol study evaluated the emission impact of the FT fuel in a newer, model year 1999 engine (DDC, 12.7 liter, turbocharged, intercooled, 321 kW @ 2100 rpm).[41] This time, the emission reductions were 37 percent in HC, 37 percent in CO, 17 percent in NO_x, and 37 percent in PM, relative to the U.S. No.2 fuel. Compared with the California fuel, FT emission were lower by 18 percent in HC, 33 percent in CO, 11 percent in NO_x, and 32 percent in PM. California-diesel emissions were matched or improved with a 50 percent FT blend in No.2 diesel. A comparison with the older, MY 1991 engine results (Figure 2-21, Figure 2-22) shows that the HC and NO_x reduction by FT fuel was smaller in the MY 1999 engine, but the PM reduction was larger. It was found that PM was reduced in the 1991 engine through reductions in both soluable organic fractin (SOF) and solid carbon, while in the 1999 engine PM was reduced primarily by carbon emission reduction alone.

Several FT emission studies on HD engines have been conducted under the auspices of the U.S. Department of Energy. The following are summaries of two such projects:[34]

- White-GMC WG64T Class 8 tractors (80,000 lb GVW) powered with MY 1996 to 1997 Caterpillar 3176B, 10.3 liter diesel engines were tested on a chassis dynamometer over the WVU 5-mile cycle.[38] The use of Shell FT fuel in place of California diesel in these trucks led to lower levels of all four regulated emissions. NO_x was reduced by an average of 12 percent, PM by 24 percent, CO by 18 percent, and THC by 40 percent.

- Six 40-foot urban buses powered by DDC 6V92 2-stroke diesel engines were operated on Mossgas FT diesel and No.2 diesel and tested on a chassis dynamometer over the CBD test cycle.[42] Three of the buses were equipped with diesel oxidation catalysts. The catalyst-equipped buses emitted an average 8 percent less NO_x and 31 percent less PM when operated on FT diesel. Emissions were reduced by 5 percent in NO_x and 20 percent in PM in buses without catalysts.

According to data published by Shell, FT fuels can provide higher, 40-60 percent emission benefit for CO, HC, and PM in light-duty vehicles, compared to only 5-30 percent range in heavy-duty engines.[43] Only small NO_x benefits were seen with FT fuels. The Shell data for different diesel engine technologies, generated over the ESC test for HD and the ECE+EUDC test for LD vehicles using CEN96 reference fuel, is listed in Table 2-8.

Table 2-8. Emission benefits for neat Shell SMDS fuel (%).

Emission	Light-Duty			Heavy-Duty		
	Euro 1	Euro 2	Euro 3	Euro 1	Euro 2	Euro 3
CO	40	53	75	22	5	16
HC	45	63	62	13	23	<9
PM	42	39	41	18	18	34...10
NOx	10	5	5	16	15	5...19

A6.   Life Cycle Analysis

From the lifecycle greenhouse gas (global warming) emission perspective, FT fuels produced from natural gas are approximately equivalent to petroleum fuels, Figure 2-23.[43] The carbon efficiency of the Shell Middle Distillate Synthesis (SMDS) process is currently lower than that of a state-of-the-art refinery. This can be offset by benefits upstream and in the vehicle usage. Some FT fuels may provide up to about 5 percent CO_2 benefit relative to petroleum diesel due to higher heat value and higher H/C ratio. As shown in Figure 2-23, FT fuels show favorable lifecycle emissions of other gases, including NO_x and SO_2.
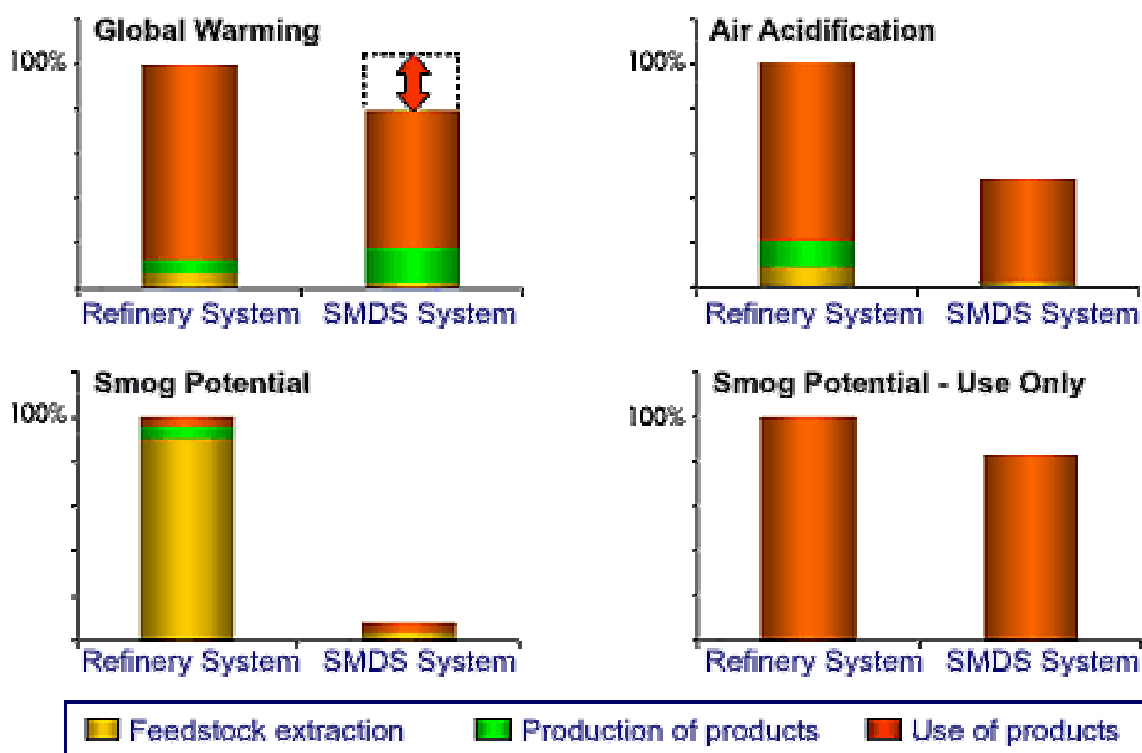
Figure 2-23. Life cycle analysis for Shell SMDS fuel.

While presenting potentially very attractive way of gas utilization, in view of the global warming concerns natural gas-derived FT fuels are not the most attractive fuel alternative for the future. However, as mentioned before, FT fuels can be produced from synthesis gases obtained from renewable biomass. Biomass-derived FT fuels, characterized by a clear CO_2 advantage, can play an important role in the future fuel market. Biomass-FT resources in the U.S. were estimated at some 25 billion gallons per annum, quite a significant figure when compared with the total U.S. distillate fuels market of 60 billion gallons.[44]

B.   Repowering With New Engine Types

Alternative fuels are being used today in place of gasoline and diesel fuel made from petroleum. The U.S. Department of Energy classifies the following fuels as "alternative fuels": biodiesel, electricity, ethanol, hydrogen, methanol, natural gas, propane, p-series, and solar energy. Using these alternative fuels can reduce dependence on imported petroleum and improve air quality.

B1.   Natural Gas (CNG/LNG)

Domestically produced and readily available to end-users through the existing utility infrastructure, natural gas has become increasingly popular as an alternative transportation fuel. Natural gas is also clean burning and produces significantly fewer harmful emissions

than reformulated gasoline. Natural gas can either be stored on board a vehicle in tanks as compressed natural gas (CNG) or cryogenically cooled to a liquid state, liquefied natural gas (LNG). Natural gas is a mixture of hydrocarbons—mainly methane (CH4)—and is produced either from gas wells or in conjunction with crude oil production. Natural gas is consumed in the residential, commercial, industrial, and utility markets. The interest for natural gas as an alternative fuel stems mainly from its clean burning qualities, its domestic resource base, and its commercial availability to end-users. Because of the gaseous nature of this fuel, it must be stored onboard a vehicle in either a compressed gaseous state (CNG) or in a liquefied state (LNG).[45]

Chemical Properties: The main constituent of natural gas is methane, which is a relatively unreactive hydrocarbon. Natural gas as delivered through the pipeline system also contains hydrocarbons such as ethane and propane; and other gases such as nitrogen, helium, carbon dioxide, hydrogen sulfide, and water vapor.

Most natural gas consumed in the United States is domestically produced. Gas streams produced from reservoirs contain natural gas liquids and other materials. Processing is required to separate the gas from petroleum liquids and to remove contaminants. First, the gas is separated from free liquids such as crude oil, hydrocarbon condensate, water, and entrained solids. The separated gas is further processed to meet specified requirements. For example, natural gas for transmission companies must generally meet certain pipeline quality specifications with respect to water content, hydrocarbon dewpoint, heating value, and hydrogen-sulfide content. A dehydration plant controls water content; a gas processing plant removes certain hydrocarbon components to hydrocarbon dewpoint specifications; and a gas sweetening plant removes hydrogen sulfide and other sulfur compounds (when present).

Natural gas is distributed throughout the United States in extensive pipeline systems that extend from the well-head to the end user. Every Continental State has access to natural gas through pipelines. The pipeline system consists of long-distance transmission systems, followed by local distribution systems. Some underground storage is also used to help supply seasonal peak needs.

According to the California Energy Commission, costs for a "slow fill" system or "quick fill" system to handle public or private fleets can range from as little as $250,000 to as much as $3 million for a bus fleet. A compressor station typically costs $2,000 to $4,000 per vehicle served. Refueling can be done easily by trained drivers. Costs for a compressor for use with a single vehicle in private homes averages about $3,500. Individual home compressors use a slow-fill system for overnight refueling. The small compressor would usually be located in a home's garage area and would be connected directly to the natural gas supply in the house.[45]

Comparing emissions, performance, and fuel economy benefits of vehicles equipped with CNG or LNG vehicle with conventional gasoline or diesel fueled engines and vehicles is a matter of intense debate and commercial competitiveness. Much of the available literature involves comparison of technologies that may not be equivalent. For instance, modern diesel engines equipped with cooled EGR and diesel particulate filter systems are compared with natural gas fueled engines that may not be equipped with oxidation catalysts or filters. Fuel economy associated with various fuels may not be representative of actual costs involved in producing the fuel, i. e., well-to-wheel cost rather than just engine fuel consumption cost.

However, some general statements may be made to highlight the main differences that are specifically applicable to natural gas fueled engines and vehicles.

Most natural gas engines available on the market today, especially in the heavy-duty category, are classified as spark-ignited, natural gas engines (SING). The compression ratio is about 11:1 and their power is controlled via throttling. Their thermal efficiency is inferior to compression-ignited, direct-injected engines (CIDI) and that leads to more fuel consumption for the CNG fueled engines. Natural gas engines are more likely to follow the homogeneous type combustion and that is characterized with lower NO_x emissions than CIDI engines. In general, CIDI engines tend to have lower levels of aldehyde emissions than natural gas engines.[45]

B2.   The Grennhouse Gases, Regulated Emissions and Energy Use in Transportation (GREET) Model

To fully evaluate energy and emission impacts of vehicle technologies, the fuel cycle from wells-to-wheels and the vehicle cycle through material recovery and vehicle disposal need to be considered. Sponsored by the U.S. Department of Energy's Office of Transportation Technologies, the Argonne National Laboratory has developed a fuel-cycle model called GREET (Greenhouse gases, Regulated Emissions, and Energy use in Transportation). It allows researchers to evaluate various engine and fuel combinations on a consistent fuel-cycle basis.

GREET was developed as a multidimensional spreadsheet model in Microsoft Excel. The first version of GREET was released in 1996. Since then, Argonne has continued to update and expand the model.

For a given engine and fuel system, GREET separately calculates the following:

- Consumption of total energy (energy in non-renewable and renewable sources), fossil fuels (petroleum, natural gas, and coal), and petroleum

- Emissions of CO_2-equivalent greenhouse gases - primarily carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O)

- Emissions of five criteria pollutants: volatile organic compounds (VOCs), carbon monoxide (CO), nitrogen oxide (NO_x), particulate matter with size smaller than 10 micron (PM10), and sulfur oxides (SO_x).

GREET (see Figure 2-24) includes more than 30 fuel-cycle pathways. It also includes these vehicle technologies:

- Conventional spark- ignition engines

- Direct-injection, spark- ignition engines

- Direct injection, compression ignition engines

       - Grid-connected hybrid electric vehicles

       - Grid-independent hybrid electric vehicles

       - Battery-powered electric vehicles

       - Fuel-cell vehicles.

To address technology improvements over time, GREET separates fuels and vehicle technologies into near- and long-term options. The latter are assumed to have improved energy and emission performance compared with the former.
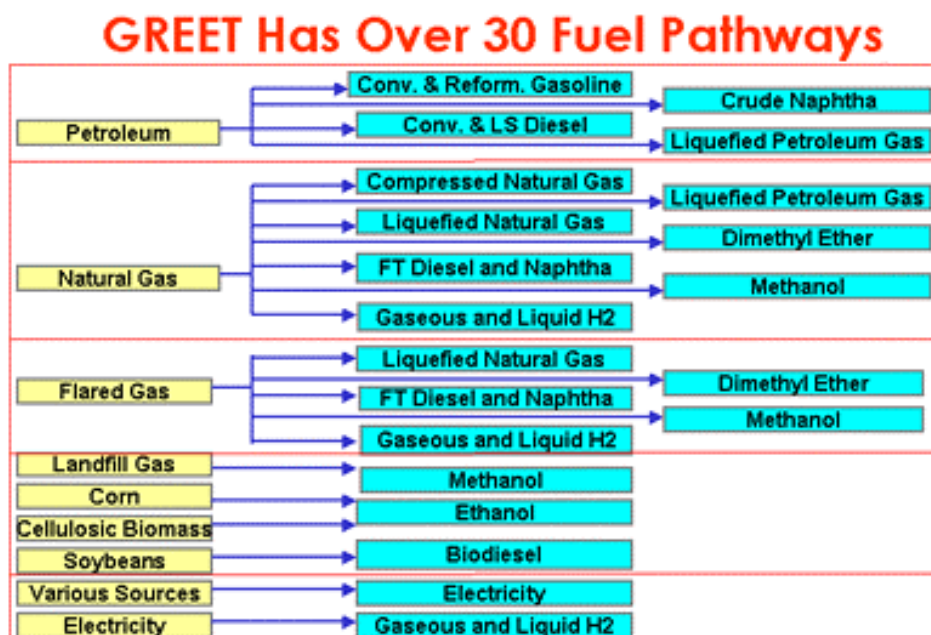
Figure 2-24. Schematic structure of the greet model.

C.   **Engine Design, Retrofit, and Add-on Technologies**

C.1.   **Engine Designs For NO$_x$ Control**

NO$_x$ emissions from heavy-duty engines were reduced by some 70 percent over the period of 1980's and 1990's. The NO$_x$ emission standards that were the driving force behind these changes are illustrated in Figure 2-25. Through the use of a combination of injection timing retard and charge air cooling, NO$_x$ emissions were eventually reduced to below 4 g/bhp-hr, as measured over the U.S. FTP Transient cycle.
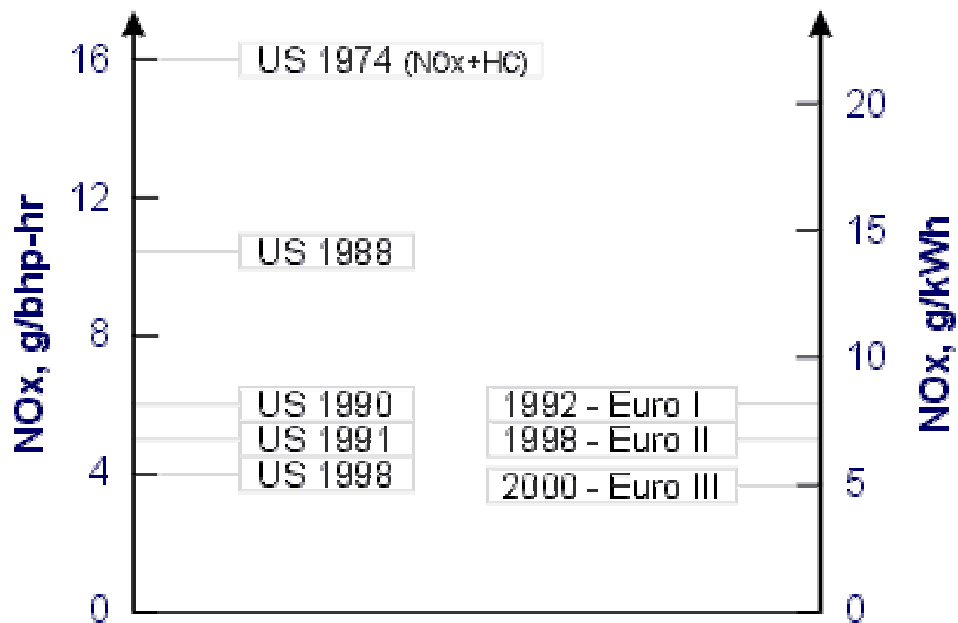
Figure 2-25. NO_x emission standards for heavy-duty engines.
(Euro I/II dates shown for engines > 85 Kw).

C.1.1. Injection Timing Retard

To better understand NO_x and its relationship to injection timing, tests were conducted on various engines to investigate the effect of engine control parameters on performance and emissions.[47] Figure 2-26 (a) shows a typical example of the effect of injection timing on NO_x emissions. A remarkably similar relationship was found by Khair, as shown in Figure 2-26 (b).[48] Note that injection timing in Figure 2-26 (a) is given as dynamic timing versus Figure 2-26 (b) where injection timing is shown as static timing. Dynamic timing for these engines was about 10° crank angle. Both references involved engines that were being developed to meet the U.S. 1991 heavy-duty emission standards and describe what was then state-of-the-art technology.

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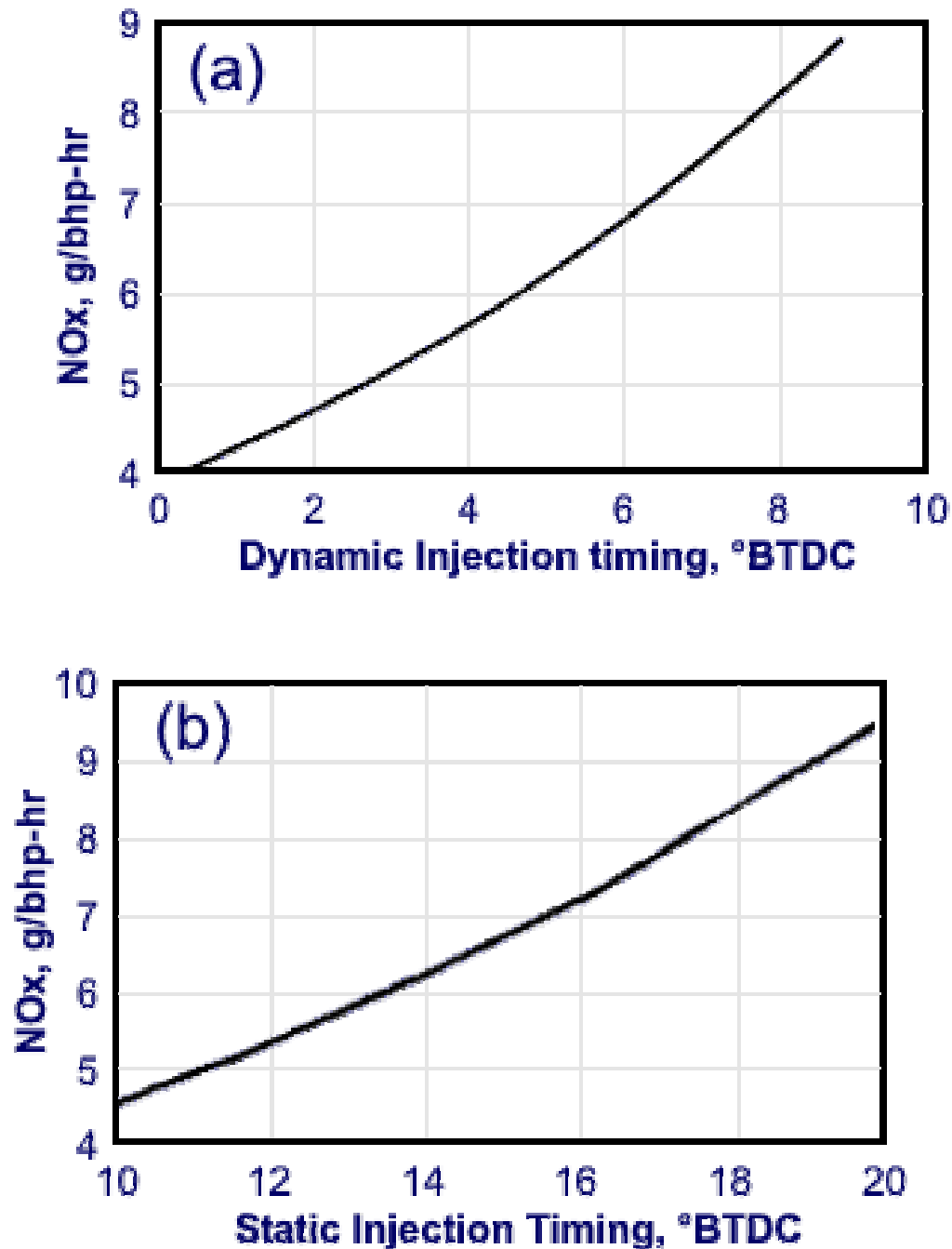
Figure 2-26. Effect of injection timing on NO$_x$ emissions.

The reason for decreasing NO$_x$ emission is shown in Figure 2-27 where a steady decrease in cylinder pressure is experienced when retarding injection timing.[47] A more detailed explanation is given in Figure 2-28 using the pressure crank angle diagram to show the directional change in cylinder pressure when retarding injection timing.[48] It should be noted that Figure 2-28 is only a schematic representation.
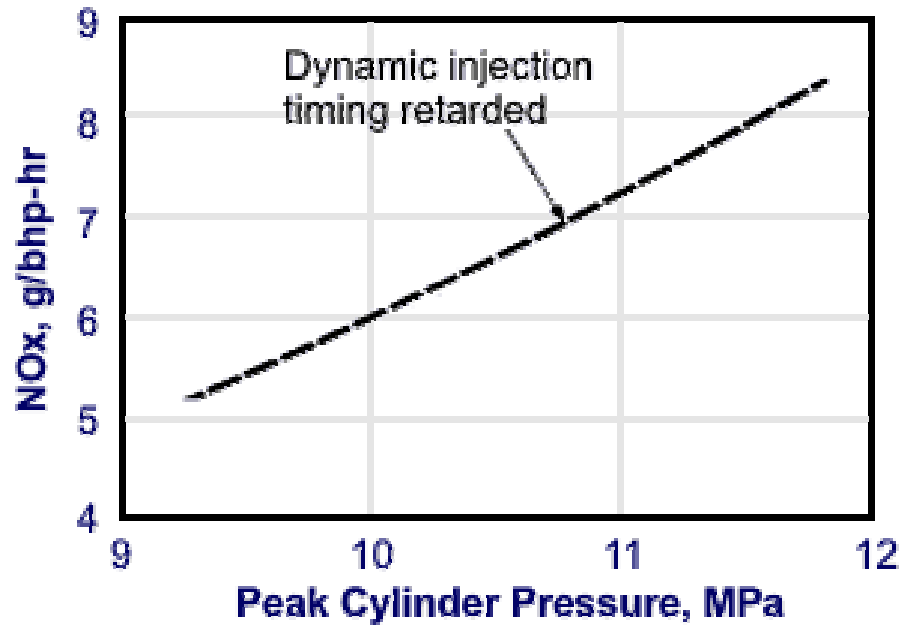
Figure 2-27. Relationship between NO_x and Peak Cylinder Pressure.
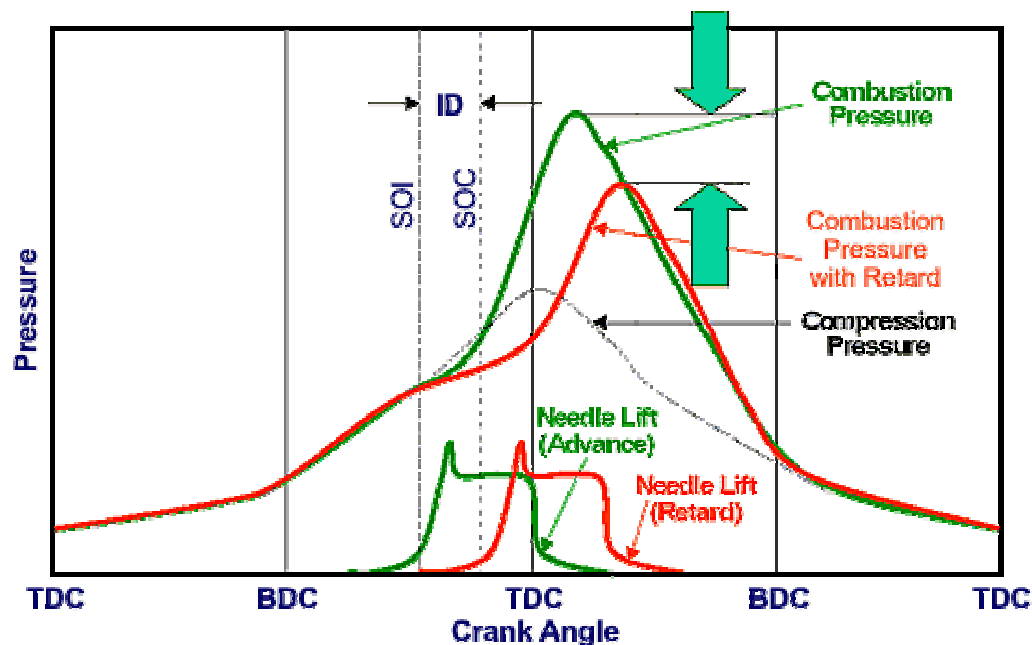
Figure 2-28. Relationship between injection timing and cylinder pressure.
(TDC - top dead center; BDC - bottom dead center; SOI - start of ignition; SOC - start of combustion; ID - ignition delay).

C.1.2. Charge Air Cooling

Cooling charge air has a similar effect on cylinder pressure as injection timing retard. However, its impact is much smaller than timing retard. Figure 2-29 is actual engine data

giving the effect of intake charge cooling, also measured in terms of intake manifold temperature, on NO_x emission.[47] Figure 2-29 is a schematic representation of the effect of intake charge cooling on cylinder pressure.[48]
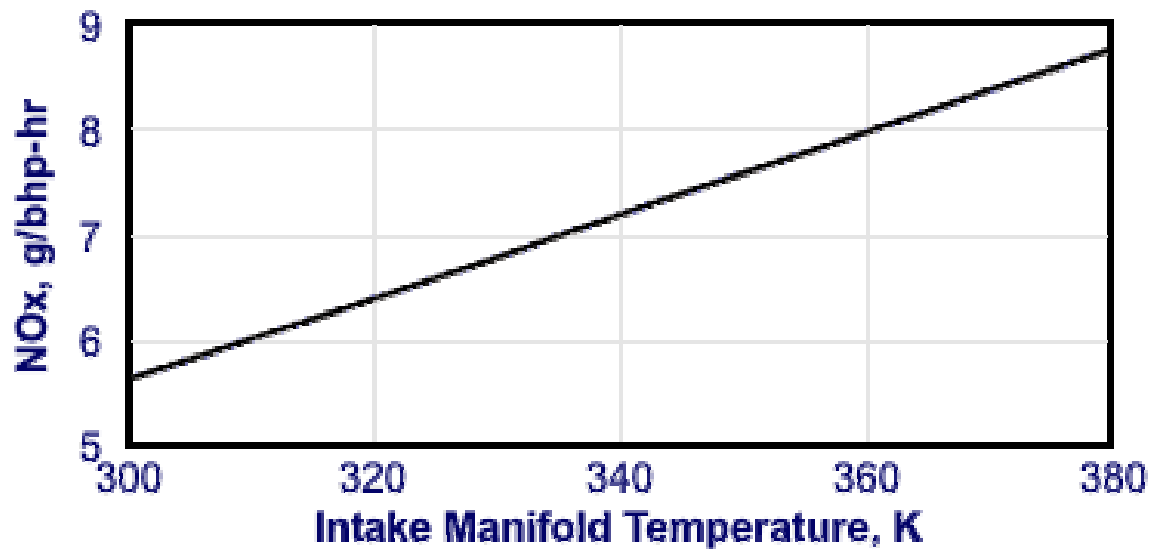
Figure 2-29. Effect of intake manifold temperature on NOx emissions.

Injection timing retard and charge air cooling, both beneficial to achieve low NO_x emissions, can be applied in combination. The mechanism at work in both cases appears to be lower combustion pressure which leads to lower peak combustion temperature and thus, lower NO_x emission. Figure 2-30 is derived from actual engine data where intake manifold temperature was controlled by varying the coolant flow in a simulated air-to-air intercooler.[49]
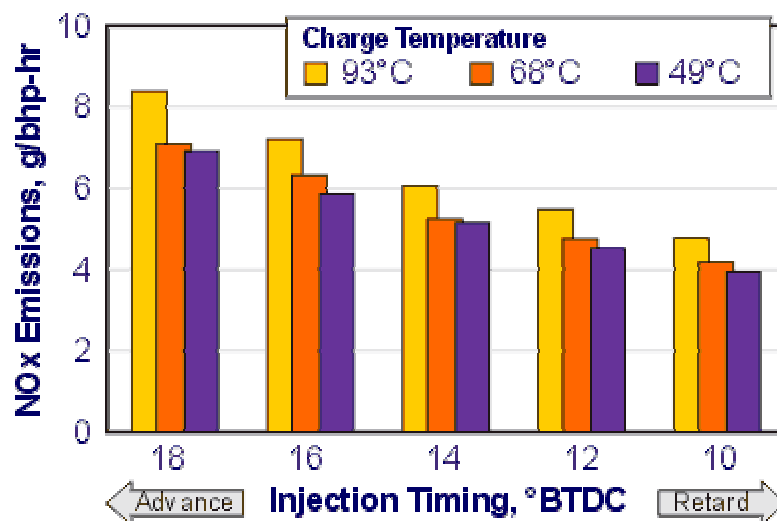
Figure 2-30. Combined effect of injection timing retard and charge air cooling on NO_x emission.

Retarding injection timing from 18° to 10° BTDC reduced transient cycle NO_x emission from about 8.5 g/bhp-hr to about 5.0 g/bhp-hr. Applying additional cooling to charge air and dropping the intake manifold temperature from 93°C to 49°C provided further NO_x reduction from about 5.0 to 4.0 g/bhp-hr.

C.1.3. Effect on Fuel Consumption

As discussed above, injection timing retard and charge air intercooling were the two actions that helped diesel engines meet NO_x standards that were in effect in the 1990's. However, if there are any reasons for the diesel engine to exist, fuel economy and durability would be at the top of the list. Conscious of this fact, engine design engineers always tried to not only preserve, but also improve the engine's fuel economy advantage. If no other measure is taken but retarding injection timing for NO_x control, substantial loss in fuel economy would be experienced. Therefore, just simply retarding injection timing is not quite acceptable for the diesel engine. Figure 2-31 shows the trade-off between NO_x emission changed via injection timing retard and brake specific fuel consumption for a medium-duty DI diesel engine.[47]
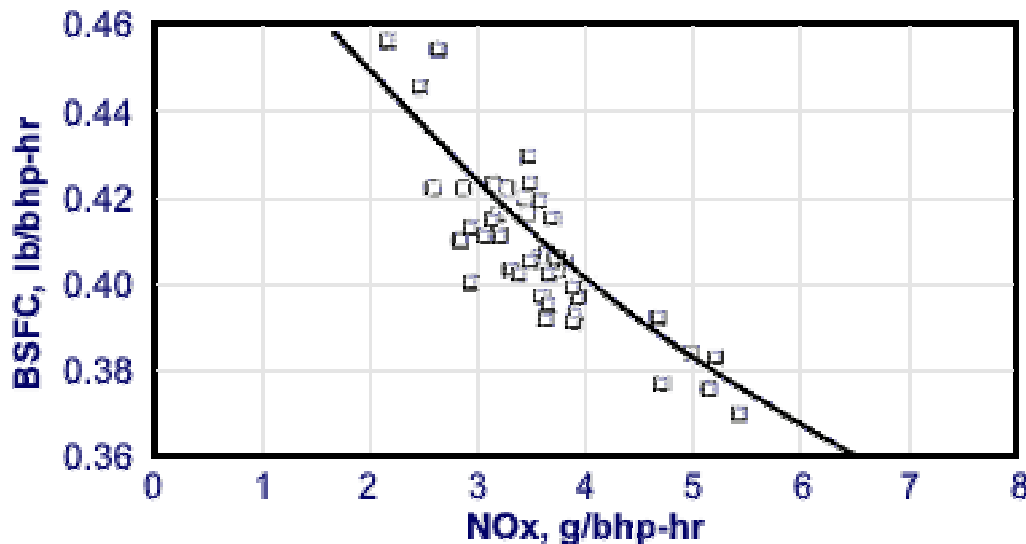
Figure 2-31. Tradeoff between NO_x and BSFC due to injection timing retard. **–** *(Rated speed and load).*

Reasons for this loss in fuel economy are attributed to the loss in peak combustion pressure that leads to reduced cycle work. To compensate for the loss of work (power) more fuel is provided to produce the desired work and this leads to more fuel consumption. It is necessary then that additional measures be taken not only to recover, but also to improve fuel economy.

Basic research showed that increasing peak injection pressure from 70 to 100 MPa (700 - 1000 bar) had a significant impact on fuel consumption. The experiment was performed at different injection timings and resulted in fuel consumption reduction at all injection timings. Since the experiment was conducted on a single cylinder engine, indicated specific fuel consumption was used to take into account increased frictional and parasitic loads of the engine accessories.

Figure 2-32 is a graphical illustration of the effect of injection pressure on fuel consumption at various NO$_x$ concentrations.
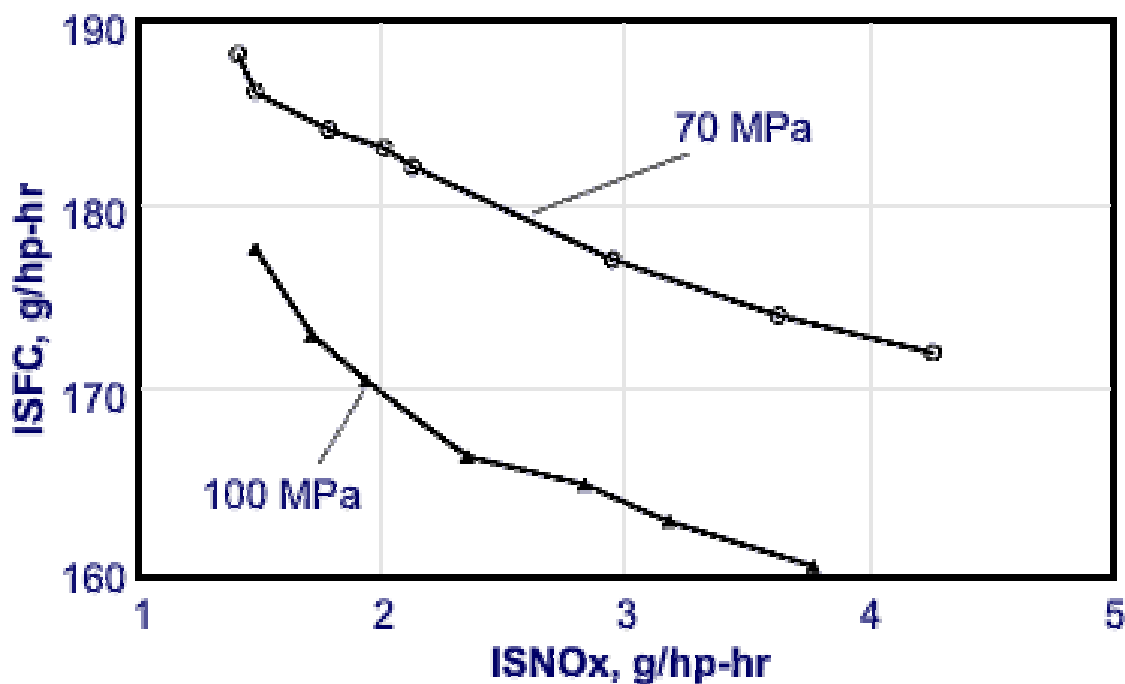
Figure 2-32. Effect of injection pressure on fuel consumption.

Applying high injection pressure in multi-cylinder engines confirmed the benefits in fuel economy that were demonstrated in single cylinder experiments. High injection pressure was obtained through faster injection cam profiles in pump-line-nozzle systems that were prevalent in the early 1990's. In addition, small hole nozzles combined with a faster cam profile helped achieve peak injection pressures in excess of 100 MPa (1000 bars). Of course, adopting unit injector systems gives the highest injection pressure potential, especially when coupled with small injection hole.

C.2. Engine Designs For PM Reduction

Since the adoption of the first US1988 emission standard for diesel particulates, through the US1994 standard of 0.1 g/bhp-hr, diesel engine manufacturers were given the task of reducing PM emissions by more than 90 percent relative to the unregulated pre-1988 levels of above 1 g/bhp-hr. In characterizing particulate matter it is common practice to distinguish between the soluble organic fraction (SOF), the insoluble (solid) fraction, and the sulfate fraction. The SOF fraction is further divided into fuel and lube oil contributions. Turning to the insoluble fraction, the major portion is dry carbonaceous soot, a product of "too-rich-to-burn" fuel combustion. However, there is evidence that lube oil also contributes to this fraction.[50] In some studies, the insoluble lube oil fraction was estimated at 5 percent of total particulate (0.02 g/bhp-hr). Finally, the solid fraction also includes wear metals and ash from the fuel and lube oil additives.

The analysis of particulate matter varies considerably depending on the engine technology and test cycle. Figure 2-33 shows an example composition, as measured on a heavy-duty engine from the discussed time period.[49] The solid fraction was found to be 47% of total PM, the total soluble organic fraction was about 41%.
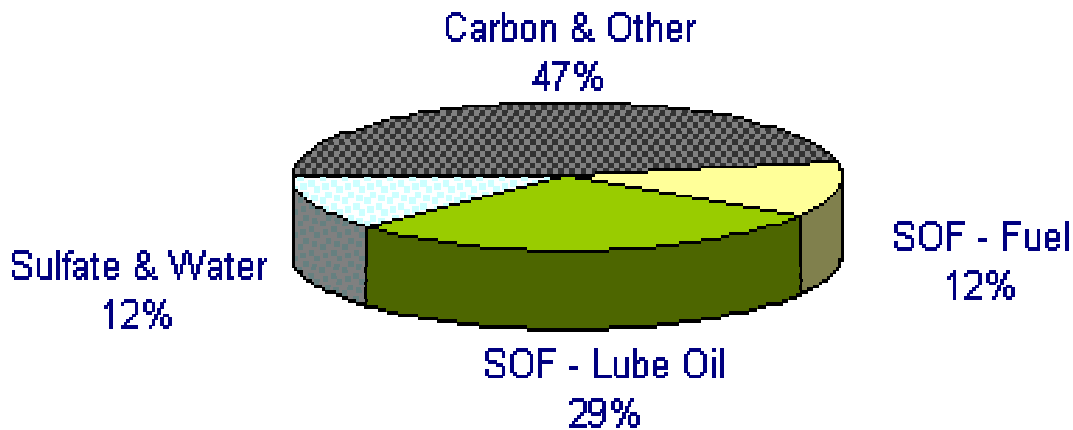
Figure 2-33. Typical PM constituents in heavy-duty 1991 engines.

Engine design techniques are focused on the control of the two major PM constituents: the solid and the soluble organic fraction. Reducing carbonaceous particulate is a task that involves more than one of the engine subsystems. For instance, without proper mixing of fuel and air, combustion efficiency is expected to suffer and carbonaceous particulate will be emitted. However, mixing of fuel and air involves both the fuel system as well as the induction system. Therefore, attention must be given to at least these two systems if we are to reduce carbon in particulate emissions. Additionally, unburned lube oil may have many sources such as cylinder bore honing, piston ring pack specifications, valve stem seals, turbocharger seals, and other miscellaneous engine components. Properly engineering these components is imperative if particulate matter is to be reduced through engine design.

It should be noted that the sulfate fraction, produced from the sulfur in diesel fuel, cannot be controlled by engine design. Introduction of more stringent PM standards may require lowering the sulfur level in fuel as a means of sulfate PM control. Such action was taken in conjunction with the US1994 emission standard, when a fuel sulfur cap of 500 ppm was established.

In the next sections, particulate matter reductions through the following systems will be reviewed:

- Air management

- Combustion

- Oil control

- Fuel injection

It must be realized that the PM control techniques were implemented in engines together with NO_x control methods. These NO_x control methods were based on injection timing retard, which worked counter productively to the PM control objective, thus making it even more challenging.

C.2.1. Air Management

Engine air management begins at the intake air filter and ends with the delivery of air into the cylinder. How charge air is managed through the entire system will have a significant impact on the products of combustion. Airflow, its temperature and pressure, as well as its kinetic energy are all important parameters to control the mixing process. The influence of turbocharger performance, charge air cooling, intake manifold design, and intake port design will be addressed as follows:

C.2.1.1. Turbocharging: Thermodynamically, turbochargers are attractive because they recover energy that would have otherwise been exhausted into the atmosphere. In turbomachinery, low pressure ratios, low air flows, and low mechanical efficiencies are associated with low engine speeds (see Figure 2-34).[51] Engine air supply is critical at low speeds if smoke and soot are to be controlled. Using a non-optimized turbocharger, at low engine speeds may not provide adequate air-to-fuel ratios to control smoke. Using a non-optimized turbocharger at high engine speeds may cause excessive swirling in the combustion chamber. This distorts the injection plumes and hurts fuel economy. For 1991, it was extremely important to maximize the air-to-fuel ratios at low engine speeds to control black smoke with increasing loads. Higher turbocharger speeds had to be limited to avoid the negative effect of over-swirling on the mixing process and to extend the turbocharger life.

To optimize the match of turbochargers to engine needs, some manufacturers used variable geometry turbochargers in their development efforts. This "flexible" device can provide a range of pressure ratios for a given engine speed. Variable geometry turbochargers can, therefore, significantly reduce smoke especially at low speed conditions. They can also improve engine output at low speeds within a specified smoke limit. Figure 2-35 shows the impact of increasing air-to-fuel ratio on full-load smoke for an engine at a fixed speed of 1000 rpm.[49] Figure 2-36 shows the fuel economy and smoke improvements at speeds below 2000 rpm.[49] These improvement were recorded at higher torque outputs made possible by the variable geometry turbocharger.
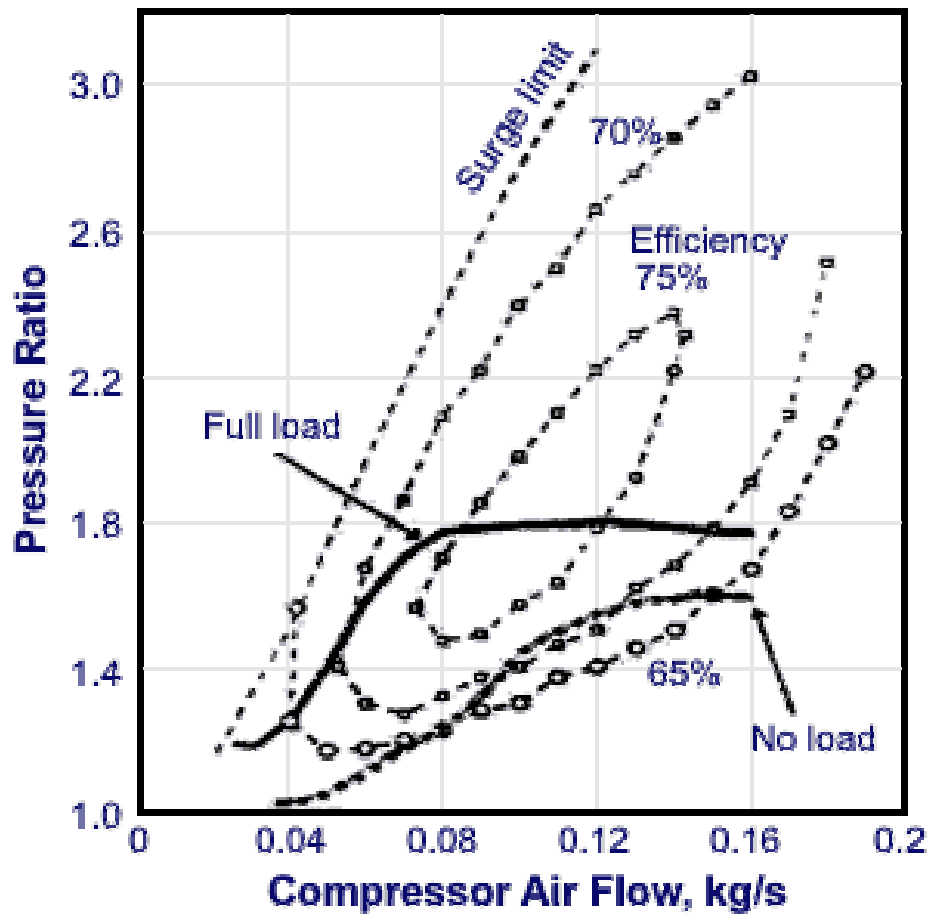
Figure 2-34. Performance characteristics of turbo-compressor.
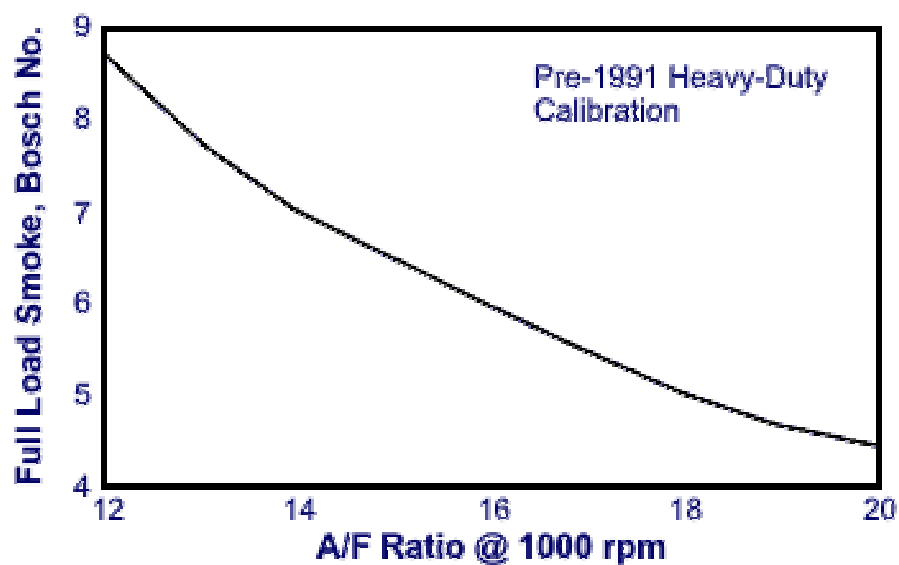
Figure 2-35. Effect of A/F ratio on full load smoke.
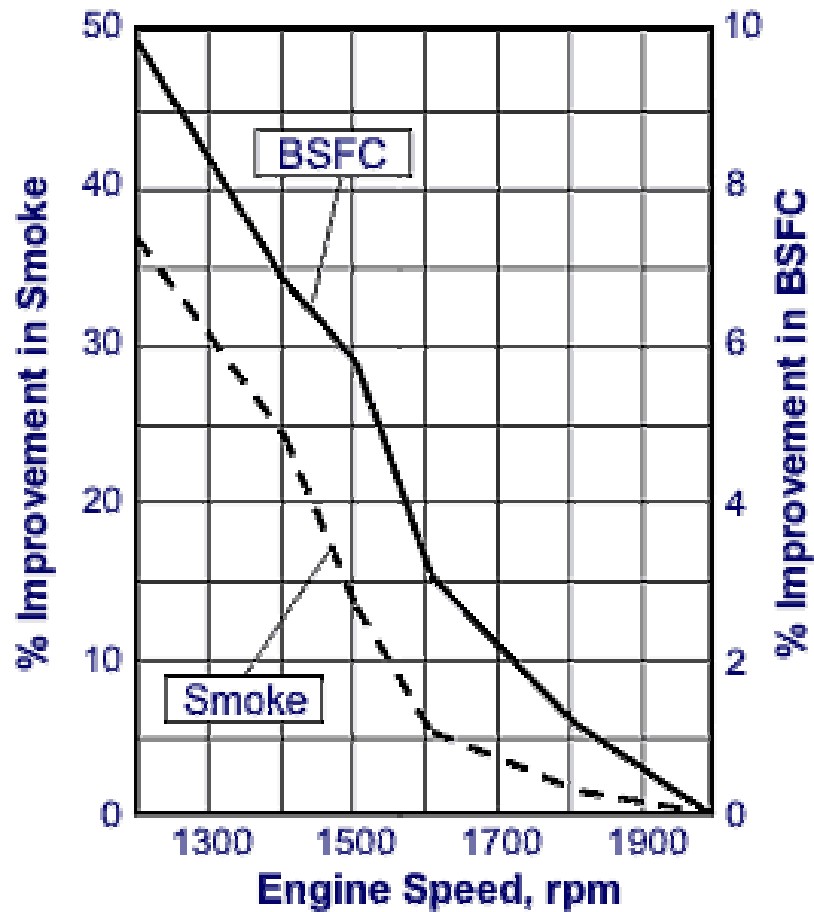
Figure 2-36. Brake specific smoke and fuel consumption improvements with variable geometry turbocharger[49].

C.2.1.2. Charge Air Cooling: Charge air cooling improves the specific power output of an engine by increasing charge air density. Benefits derived from this improved specific power output are better fuel economy and reduced exhaust emissions. Prior to the 1990's, most aftercooled (for purposes of this paper aftercooling and intercooling are used interchangeably) engines utilized jacket-water cooling where charge air temperatures were thermostatically-controlled to about 90°C (195°F). Figure 2-37 is an illustration showing a water heat exchanger installed in the intake manifold of a 7.8 L, 210 hp medium-duty DI diesel engine. However, for the 1991 engines the use of air-to-air aftercooling (see Figure 2-38) became quite popular for medium-duty and heavy-duty diesel engines, and some light-duty engines included air-to-air intercooling in production. Figure 2-39 shows the improvement in fuel economy associated with three charge air temperatures (49, 68, 93°C).[48] These temperatures were selected to represent a water jacket aftercooled engine, an engine with intermediate charge air temperature, and an air-to-air aftercooled engine, respectively. By adopting air-to-air intercooling, intake manifold temperatures of 14 to 19°C (25 to 35°F) above ambient were achieved which led to higher air densities. Air-to-air aftercooling also reduces the thermal loading of the engine by limiting combustion temperature extremes.
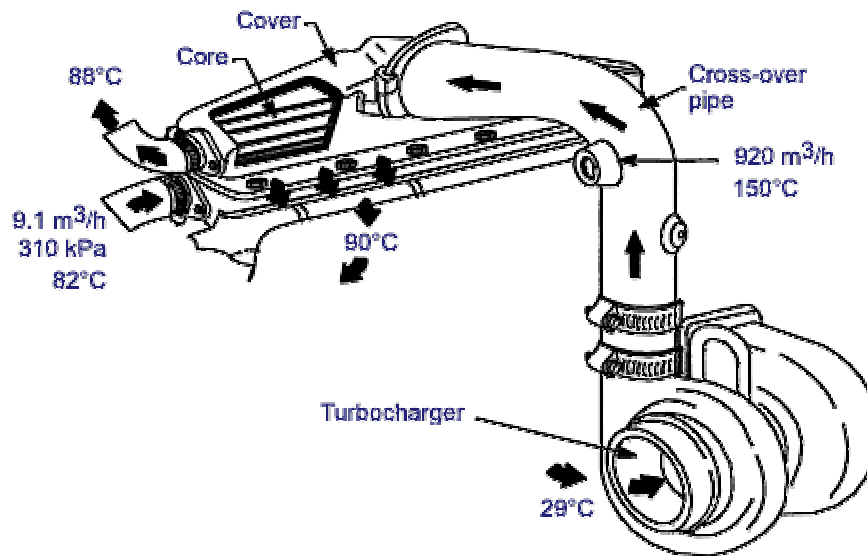
Figure 2-37. Jacket-water cooling of charge air.
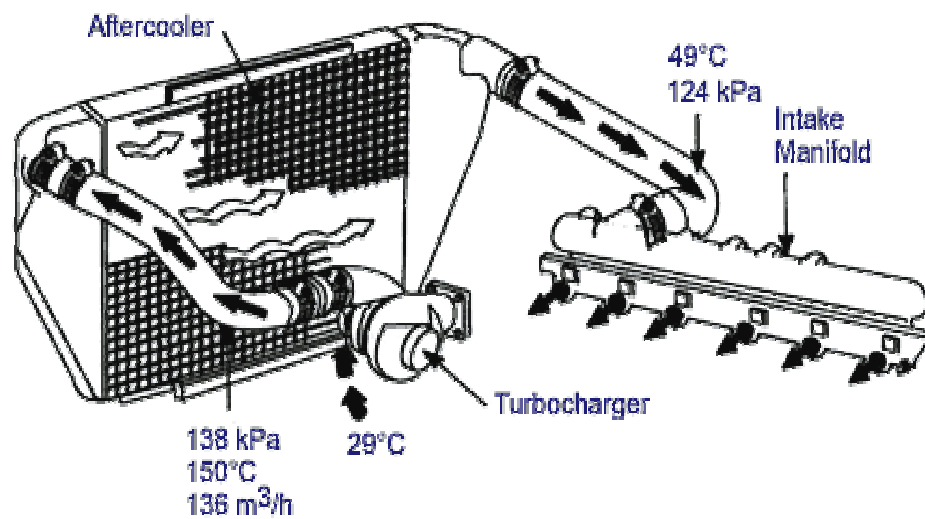
Figure 2-38. Air-to-air charge air cooling.
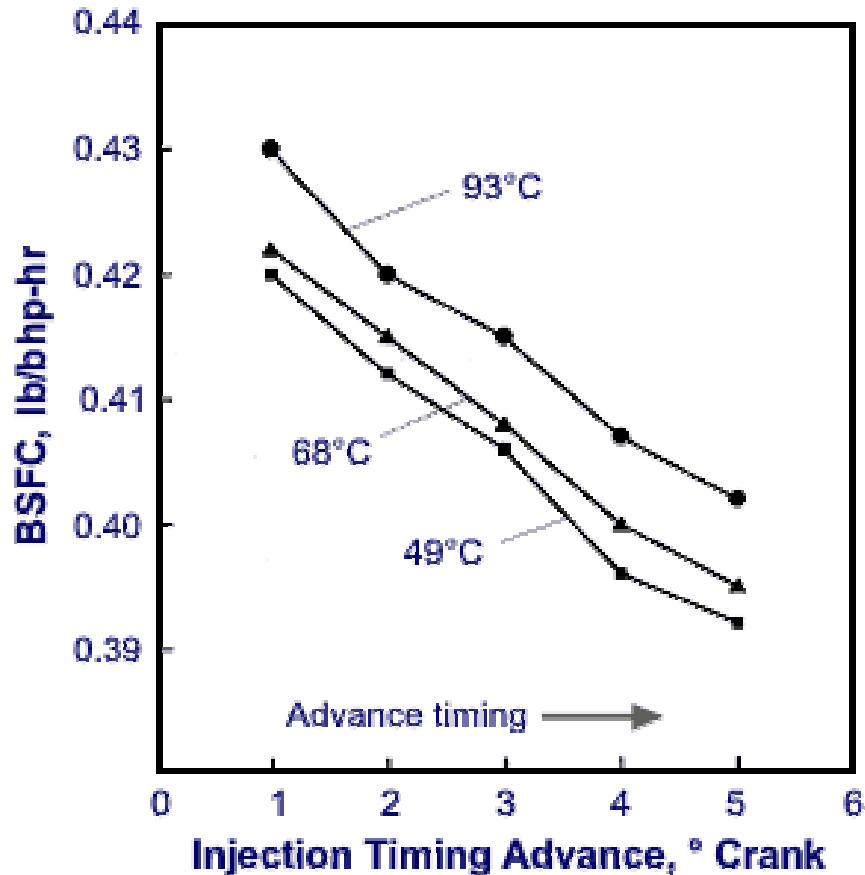
Figure 2-39. Effect of charge air temperature and injection timing on transient cycle fuel consumption.

The net effect of low temperature charge air cooling was increased air density that led to increased mass of air available to the combustion process and increased particulate oxidation. In addition, lower intake manifold temperature led to lower peak cylinder pressure and temperature. Lower fuel consumption associated with low temperature charge air cooling indicates that more of the fuel is converted into brake power, i. e., the unburned fuel fraction is reduced as well as its corresponding particulate matter.[52]

C.2.1.3. Intake Manifold: While it is difficult to relate intake manifold designs to particulate matter, they do contribute to good mixture preparation, without which combustion may be incomplete, leading to considerable particulate emissions. In fact, in a multi-cylinder engine, charge air maldistribution in just one cylinder can create a poor mixture in that cylinder and produce heavy smoke and particulate emissions that would reflect on the entire engine.[48]

Although intake manifolds appear to be simple components, they play a major role in engine performance and deserve careful attention from engine designers. It is important for the intake manifold to distribute the air evenly to the cylinders. Considerable bench testing and development led to intake manifold designs having even flow distribution to all cylinders with minimum pressure losses. The intake port shape and manifold design are often tested as a total system rather than two separate components. In some cases, effort was expended in reducing the impact of consecutive intake valve openings on the pressure waves in the intake

manifold. Segmenting the intake manifold, then grouping certain ports to the proper manifold segment can prevent the interference of unsteady airflow into the combustion chamber.[48]

C.2.1.4. Intake Port: The mixing of fuel and air in a diesel engine has a very strong influence on its performance and emission characteristics. Diesel emission control engineers are always challenged with the fuel and air management to achieve optimum performance. Flow bench fixtures are used to select intake port designs that impart good swirl or air rotation while maintaining good breathing quality.[53]

C.2.2. Combustion System Design

C.2.2.1. Combustion Bowl Shape: A key point in designing the combustion bowl is that good mixing of fuel and air is achieved. Turbulence in the air motion within the combustion bowl is found to be beneficial to the mixing process. Swirl induced by the intake port can be enhanced to create more turbulence during the compression stroke through proper design of the crater, or bowl in the piston crown.[49]

C.2.2.2. Combustion Bowl Location: In combustion systems featuring two-valve designs (one intake and one exhaust valve), injectors are usually installed at an angle as shown in Figure 2-40. The inclination angle of the injector is dictated by the many cavities in the cylinder head. Positioning the injector at an angle results in non-symmetry in nozzle hole drilling to ensure the fuel is sprayed in the combustion bowl. In addition to the non-symmetrical drilling of the nozzle holes, the combustion bowl has to be offset from the center of the cylinder bore to allow for concentricity between the nozzle tip and the combustion bowl. The lack of symmetry in drilling the nozzle holes leads to uneven spray lengths as shown in Figure 2-40 that in turn leads to uneven utilization of the compressed air in the combustion bowl.[54] Moving towards the modern diesel engine design, two-valve combustion systems attempted to reduce the offset between the center of the combustion bowl and the cylinder bore for better air utilization, lower HC, CO, and PM emissions. Ultimately, for best symmetry and spray distribution, a centrally located, vertically installed injector should be the goal for lowest HC, CO, and PM emissions.[48,49]

It is true that this and other technologies already mentioned may not be amenable to retrofitting existing fleets, however, they are mentioned in this report for completeness. Much more can be said about each of these technologies, but their description and details are kept to a minimum since they pertain more to original equipment manufacturers than retrofit applications.
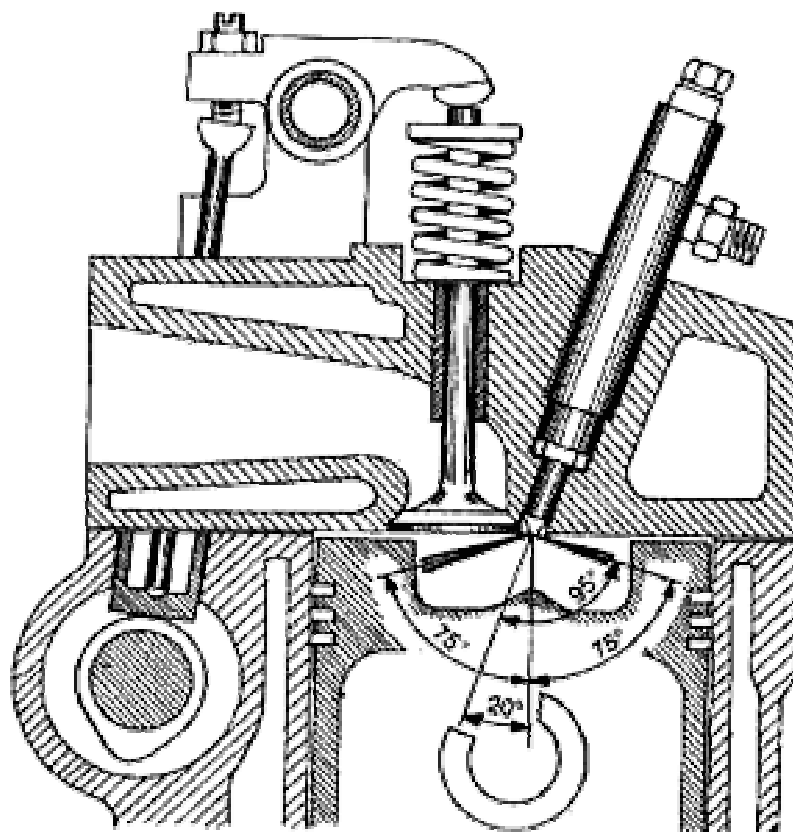
Figure 2-40. Injector installation and combustion bowl offset in two-valve combustion systems.

C.2.2.3. Compression ratio is another engine design parameter that impacts emission control. In general, higher compression ratios cause a reduction in PM emissions and improved fuel economy, but also cause an increase in NO_x emissions. However, higher compression ratios require a stronger engine structure, which may increase weight and cost. The increased engine weight and frictional losses somewhat offset the fuel economy benefit of higher compression ratios, especially at very high compression ratios. Conversely, lower compression ratios generally cause a reduction in NO_x emissions, while causing an increase in PM emissions and decreased fuel economy. In addition, lower compression ratios lead to cold-starting difficulties.[55]

By raising compression ratio, ignition delay is reduced which in turn reduces the premixed portion of the fuel and allows more injection timing retardation to control NO_x while maintaining good NO_x/BSFC trade-off. White smoke problems are often aggravated by a combination of retarded injection timing and colder charge air. Raising the compression ratio from the 16.5:1 to 18.5:1 leads to significant reductions in white smoke especially in cold start and warm up operation.

C.3. Oil Consumption Control

Various investigations carried out have demonstrated that lube oil is a significant contributor to diesel particulate emissions.[56,57] In fact, for diesel engine designs of the early 1990's, lube oil particulate fraction eventually determined whether the particulate standard were met or not. To achieve low oil consumption it is necessary to control oil in three major areas:

- Cylinder wall

- Intake and exhaust systems

- Lube oil formulation

The first of these three areas has always been considered by engine manufacturers during their design and development phases. Lube oil formulation as it relates to oil consumption control continues to be a cooperative task between lube oil and engine companies. Discovery of the lube oil impact on particulate emissions added more emphasis on its formulation and as more stringent emissions are mandated this trend is expected to continue. Highest on the priority list of oil consumption control is the attention given to the cylinder wall area. This area is by far the most involved and entails several technologies and component design interactions that are summarized in Table 2-9.[58]

Table 2-9. Criteria and design parameters affecting lube oil consumption from the cylinder wall area.

Oil Consumption (Cylinder Wall)	**Bore Distortion**	Block Liner Head Gasket
	Cylinder Surface Profile (Oil Carrying Capacity)	Material Properties Honing Process Roughness
	Lube Oil Evaporation Characteristics	Cylinder Wall Temperature Flame Contact with Oil Distillation Range of Lube
	Liners, Rings, Ring Grooves Wear	Material Properties Heat Treat Piston/Ring Design Ring Motion Transverse Piston Motion
	Scraping of Piston Rings	Ring Face Profile Ring Tension Ring Geometry/Compliance
	Piston Ring Movement	Ring Land Geometry (Pressure Balancing) Ring/Groove Clearance Piston Transverse Movement
	Transverse Piston Movement	Piston Structure Piston Skirt Profile Piston Skirt Softness Piston Pin Offset

The parameters included in that chart give us an idea of the immensely difficult task of designing pistons, piston rings, cylinder liners, combustion systems, and manufacturing processes that work in concert to reduce oil consumption while at the same time achieve performance and emissions objectives. Cylinder bore distortion has a predominant effect on oil consumption and its importance is emphasized. Usually, advanced finite element techniques are used to minimize bore distortion, thereby minimizing its influence on lube oil consumption.

C.3.1. Piston rings are used to seal the combustion gases within the combustion chamber, assist in heat transfer from the piston to the cylinder wall, and control lubrication in the cylinder wall area. Typical piston ring pack designs incorporate three or more rings:

- A top compression or fire ring

- One or more secondary compression rings

- One or more oil control rings

The need for a second compression ring is dictated by the ring gap that is necessary for ring installation. Normally, ring gaps from consecutive rings are staggered to avoid creating a leak path from the compression volume to the crankcase. In general, it is preferable to minimize the total number of rings since they are a major source of friction. Major influences to piston ring design include ring bearing face and side wear, fatigue fractures, thermal resistance, and dynamic characteristics.[52] Piston rings are designed to closely fit in piston ring grooves to minimize gas leakage, or blow-by, and to properly meter lubrication. To minimize wear and to prevent excessive oil consumption or undesired lubricant contribution to combustion emissions, piston rings and their grooves are designed to minimize ring sticking and optimize ring dynamic motion. Piston ring design is very complex and a vast body of knowledge has been generated over the years on all aspects of their design.

Piston rings seal the combustion chamber by contact between the piston ring face and the cylinder wall and the ring sides and the top or bottom of its groove. This contact is the result of forces from the spring action of the ring and the combustion gas pressure behind and on top of the ring.[52] The spring forces, called the contact pressure, depend on the ring material and dimensions, the camber, or circumferential profile, and the size of the free, or uncompressed, gap in the ring. The contact pressure can either be constant or variable depending on the camber, and should be minimal to prevent excess frictional losses. Typically, uniform contact pressure is desired for all engine operating conditions. However, due to thermal distortion of the rings and cylinder liner, or special considerations such as liner ports in two-stroke engines, variable contact pressure are specified at room temperature. In all cases, the ring should not have an opening between the ring face and the cylinder wall when installed in the cylinder, a specification known as "light tight". Ring stress calculations are normally conducted to ensure opening and closure stress are below material limits when the ring is opened to slip over the piston and compressed to enter the cylinder. There are five basic types of compression ring cross-sections and two basic oil control ring types. The compression ring cross-sections are rectangular, taper faced, keystone, internally beveled, and L-shaped. The rectangular ring is geometrically simple, thus less expensive, and provides sufficient seal for most applications.

While piston ring design is complex and requires substantial experience, it is further complicated by bore distortion. Attempts to make piston rings light-tight at room temperature do not guarantee the same fit at high temperatures to which they are exposed at operating engine conditions. Once again, experience is supplemented with advance finite element analysis to predict the shape of piston rings within distorted bores.

C.3.2. Liner Surface Finish is very critical to engine durability as well as oil consumption. Honing of the liner ID is conducted to achieve the proper surface finish. Correct honing produces a cylinder liner surface finish that exhibits a crosshatch pattern similar to that illustrated in Figure 2-41, which shows a 20° to 25° and a 40° to 50° example. Each engine manufacturer specifies in its service manual what angle of crosshatch pattern and what surface finish are desired.[52]
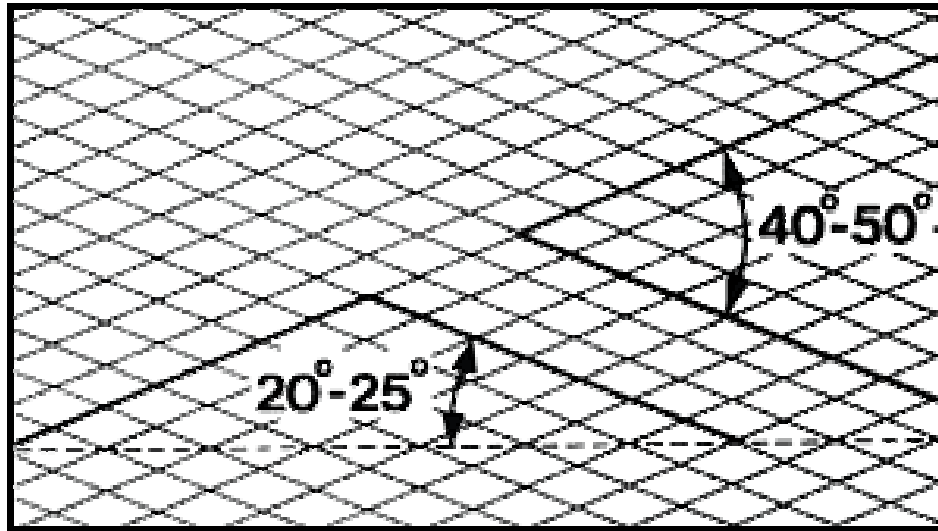
Figure 2-41. Amplified example of microfinish surface.

Surface finish is usually stated as being in the region of 20 to 35 RMS (root mean square), which is simply a mathematical term indicating the average irregularity in millionths of an inch (0.000001 inch). The actual microinch surface finish is controlled by the proper selection of honing stone used (grit). It is worth noting that the rougher the stone grit used, the larger the microinch surface finish and the higher the oil consumption as well as its contribution to PM emission.

C.3.3. Intake and Exhaust Systems: The second major source of oil contribution to particulate emission is through the intake and exhaust systems. At first glance this categorization may seem rather unusual, however significant leakage paths contribute lube oil through the intake and exhaust systems. For instance, valve stem seals, both on the intake as well as the exhaust sides can cause lube oil intrusion in the intake or exhaust ports. Turbocharger seals are often the source of lube oil in the intake manifold. Blow-by returned into the inlet system is another potential source of oil-based contribution to the particulate problem.

C.3.4. The formulation of lube oil to assist in meeting the very strict emissions requirements is the last of the factors affecting oil consumption. This topic does not only affect engine durability, but also impacts future use of post-combustion exhaust emission control devices such as diesel oxidation catalysts.[58] Therefore, developing new lube oil formulation has to be carried out in close cooperation between engine and oil companies.

C.4.   Fuel Injection System

Considerable effort has gone into the development of the fuel injection system. Components had to be selected and carefully matched to the combustion system. Although many of the parameters discussed in this section were addressed earlier, the following fuel system variables are reviewed here with the focus on their role in PM control:[59,60]

-   Injection timing

-   Injection pressure

-   Injection duration

-   Nozzle hole configuration

C.4.1. Injection Timing: Injection timing was the most effective tool for reducing NO_x emissions. Unfortunately, injection timing retard conflicts with good fuel economy and low particulate emissions. To reduce the fuel economy penalty associated with retarding injection timing, measures are adopted to reduce ignition delay such as using high compression ratio and higher injection pressures.[59,60]

C.4.2. Injection Pressure: The effect of injection pressure on engine performance and emissions has been recognized since the early seventies. However, some manufacturers felt that injection rate shaping was more effective in reducing emissions than injection pressure. A large body of work in this area has been published.[47] Changes in injection pressure affect the rate of fuel injection, injection duration, atomization, and spray penetration. Therefore, it is very difficult to separate the effect of injection pressure alone from that of rate shaping. Studies conducted to investigate this subject show that increasing injection pressure leads to improved fuel economy and smoke characteristics, Figure 2-42. For diesel engines designed for the early 1990's, full-load rated speed injection pressure were between 100 and 120 MPa (1,000 - 1,200 bar) versus pre-1990's level of 65 to 70 MPa (650 - 700 bar).
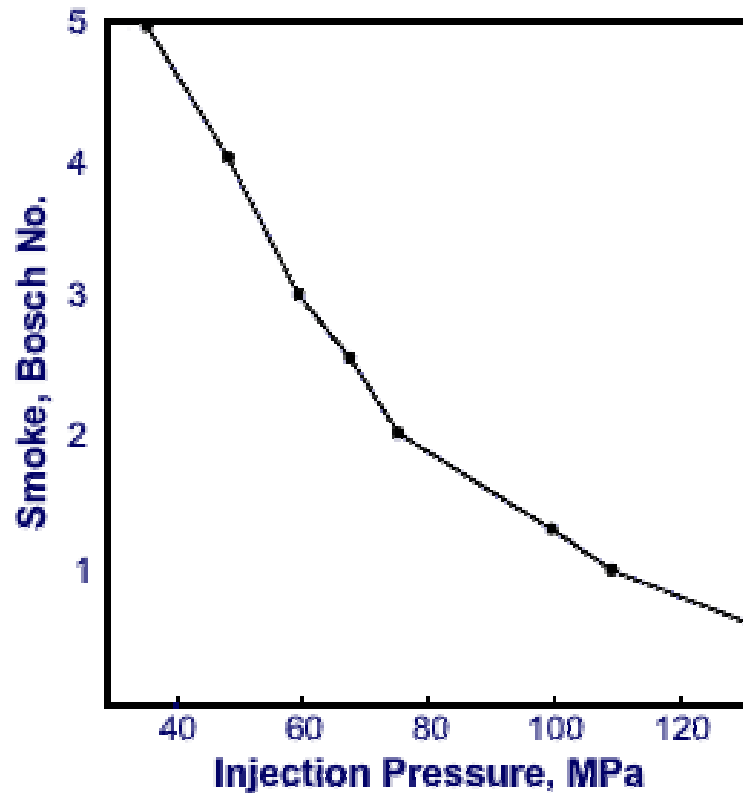
Figure 2-42. Effect of injection pressure on smoke emissions.

C.4.3. Injection Duration: Injection durations were traditionally extremely short and injections were designed to be completed close to TDC where maximum combustion efficiency could be realized. With the introduction of new combustion developments, more emphasis was placed on the proper matching of injection duration to the combustion system. Engines equipped with swirl-supported combustion systems, an injection duration at rated speed and load conditions of approximately 25° to 30° crankangle was found to be optimum.[49] Of course, this by no means suggests that injection duration is an independently controlled parameter. It is, however, a product of several choices related to the injection system and engine power output. These choices include nozzle hole size, number of nozzle holes, injection pressure, engine speed, and injected fuel quantity.[49]

C.4.4. Injector Nozzle Configuration: The injector nozzle is the point of fuel delivery to the combustion chamber. Its design and placement in the cylinder head (angle of inclination) are of paramount importance to engine performance and emissions characteristics. Several parametric studies have been conducted and led to the following generalized statements describing optimized components of the nozzle configurations for the 1990's direct injection swirl-supported engines:

Nozzle sac volumes must be reduced to a minimum. In most cases the so-called cylindrical sac (shown in Figure 2-43) was adequate, but in some cases a conical design was necessary. Conical sac volume is much less than its cylindrical sac counterpart resulting in reduced nozzle dribble and its associated particulate emissions.[49]

Cylindrical sac   **Conical sac**
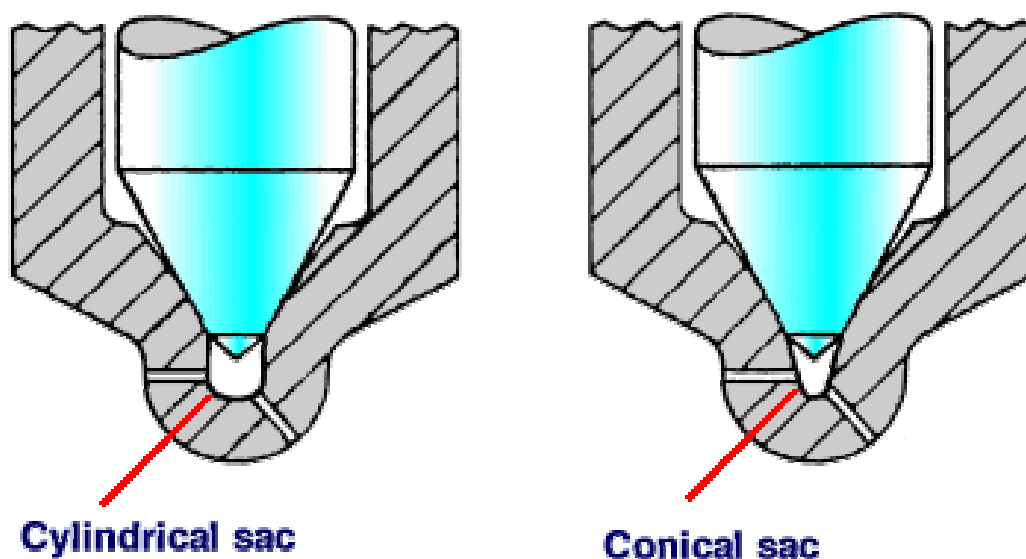
Figure 2-43. Comparison between cylindrical and tapered (Conical) sac volumes.

The length of the nozzle hole must be chosen for its contribution to fuel spray penetration which together with proper atomization helps in maximizing air utilization. In general, the optimum hole length was found to be 2.7 times the hole diameter. The spray cone (included) angle must be selected with regards to the specific combustion bowl design. A significant amount of interaction exists between the various parameters already mentioned. The effect of some of these variables can readily be seen.[49]

The above review of the fuel system components and their characteristics for the 1990's engines is by no means a comprehensive account of all the changes. Some very important choices were made in the areas of injection in-line pump delivery valves, high pressure injection lines, and the number and size of spill ports. In addition, shaping the torque curve between peak torque and rated speed, and the selection of a smoke limiting devices were especially important in reducing emissions.

C.5.   Exhaust Gas Recirculation

C.5.1 Principle of Operation

Exhaust gas recirculation (EGR) is a method by which a portion of engine's exhaust is returned to its combustion chambers via its inlet system, as shown in Figure 2-44.[61] This method involves displacing some of the oxygen inducted into the engine as part of its fresh charge air with inert gases, thus reducing the rate of NO_x formation. EGR may be also designed to absorb heat from the combustion process, thus lowering its temperature and reducing NO_x (although at some engine conditions, especially at high loads, EGR actually may increase the combustion temperature).
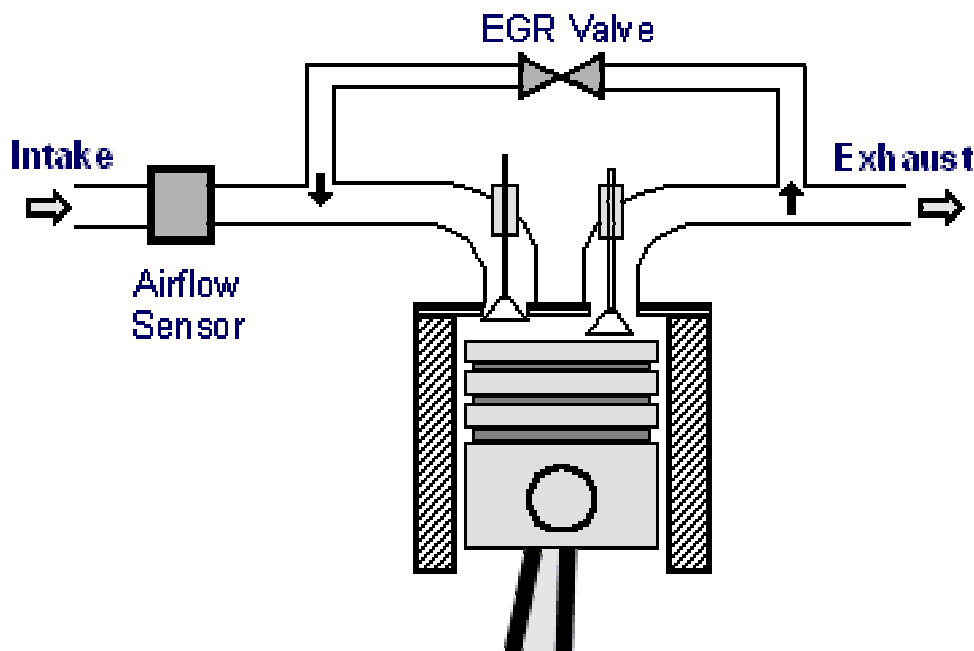
Figure 2-44. Schematic representation of exhaust gas recirculation.

Exhaust gas recirculation is certainly not a new technology for gasoline or light-duty diesel engines.[62] However, its application in heavy-duty diesels was not required until the US 2004/2002 emissions limits were introduced. With the prospect of tighter heavy-duty diesel NO$_x$ limits of 2.0 g/bhp-hr (2.7 g/kWh), engine manufacturers have been developing sophisticated EGR systems for NO$_x$ control in direct-injected engines. It has been shown that EGR is a very effective method for NO$_x$ reduction.

In general, two principles are believed to be responsible for the NO$_x$ reduction effect of EGR, as follows:

    -Dilution of the intake air with inert gases, leading to a decrease of oxygen concentration in the combustion process.

    -Heat absorption by the EGR stream, primarily due to the heat absorbing capacity of CO$_2$ (thermal effect), as well as through the dissociation of CO$_2$ (chemical effect), leading to a reduction in combustion pressures and temperatures.

It is now believed that the intake air dilution is the dominant NO$_x$ reduction mechanism. The other effects, once suspected to play an important role, are considered to be less significant.[62] However, the relative significance of NO$_x$ reduction mechanisms depends on the particular application. For example, the role of the heat adsorption mechanism will be more pronounced in systems where the EGR stream is cooled prior to mixing with the intake air. The *heat absorption* principle is that of reducing peak combustion temperatures where EGR acts as a heat sink.[63] In this case, the heat absorbed by EGR is thought to be directly proportional to the product of EGR flow rate, the specific heat at constant pressure, and the temperature differential between combustion temperature and that of the EGR. Combustion products consist mostly of CO$_2$ and H$_2$O with specific heats higher than those of air. At

standard temperature and pressure conditions, the specific heat (c_p) of CO_2, H_2O, and N_2 amounts to 36.0, 33.5, and 29.2 kJ/kmol·K, respectively (it is customary to express EGR ratios volumetrically; assuming ideal gases, volumetric and mole units are proportional).[64]

The second and more important principle by which EGR reduces NO_x emissions is displacing some of the oxygen induced with the fresh air charge.[63] Thermal NO_x is formed from nitrogen and oxygen under thermodynamically favorable conditions. The final level of NO_x emission also depends on the residence time of the reactants in the combustion chamber (T_r). Controlling any of the basic variables (N_2, O_2, T_{comb}, and T_r) would control the rate of NO_x formation. Therefore, reducing the fresh charge air oxygen content by means of EGR reduces NO_x formation through reducing O_2, T_{comb}, or T_r, all of which contribute to NO_x formation.

One of negative consequences of using EGR is its adverse influence on particulate matter emission. A test conducted on a Series 60, 11 L, turbocharged, and intercooled Detroit Diesel engine where EGR was systematically increased from Level A through D (Figure 2-45) shows the corresponding Total PM (TPM) emission increase during a series of EPA heavy-duty transient tests.[65]
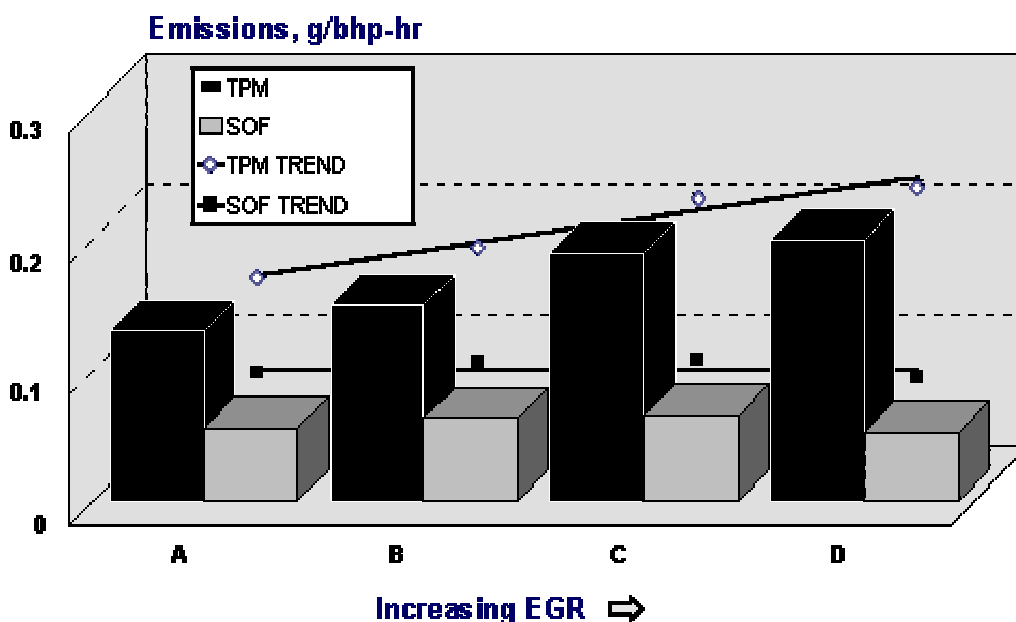
Figure 2-45. Effect of EGR on particulate emissions.

Analysis of the particulate samples indicated that the soluble organic fraction (SOF) remained constant. It was also concluded that the insoluble fraction (mostly carbonaceous) of the particulate increased as EGR rates increased from A to D. Oxidation type catalytic converters were designed to reduce particulate SOF, and unfortunately, do not curb the insoluble fraction. Diesel particulate filters (DPF) are a very effective aftertreatment alternative to control the insoluble PM fraction on EGR engines in applications where very low PM emission levels are required.

C.5.2. Types of EGR Systems

From Figure 2-44, it is implied that a pressure differential exists between the exhaust and intake manifold without which EGR could not flow from the former to the latter. In turbocharged heavy-duty diesel engines it is sometimes difficult to introduce EGR into the intake manifold. The problem is that intake manifold pressures are usually greater than exhaust system pressures. [66] To circumvent this dilemma exhaust is intercepted at a point upstream of the turbocharger (see Figure 2-46) where pressure is higher than that of the intake manifold. A portion of the exhaust flow is returned to the engine cylinders through an electronically-controlled EGR valve after being cooled as shown in Figure 2-46. This approach is commonly referred to as high pressure loop (HPL) EGR.
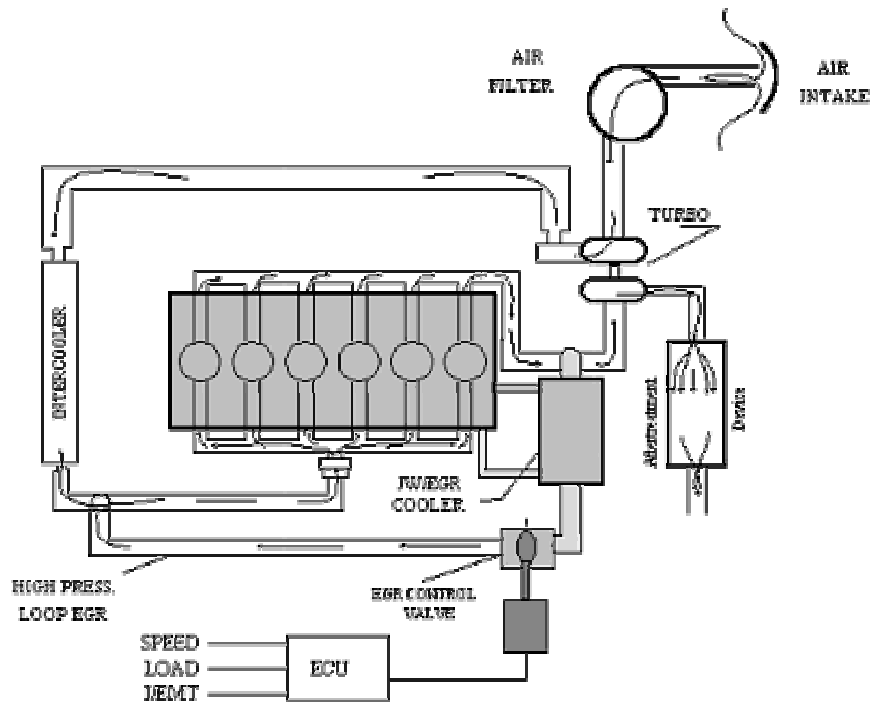
Figure 2-46. Schematic representation of HPL EGR system.

High pressure loop EGR applied to several heavy-duty diesel engines has enabled NO_x reduction to the US FTP level of 2.0 g/bhp-hr. The penalty associated with such a system, however, was a recorded increase in fuel consumption and an associated increase in particulate matter emissions. In HPL EGR implementations, turbocharger matching is usually revised to compensate for losing turbocharging effectiveness when a portion of the exhaust is intercepted and its energy rerouted away from the turbine wheel.

To increase the pressure drop between the exhaust and intake manifolds, thus facilitating EGR flow into the engine inlet duct, some have utilized a venturi, as shown in Figure 2-47.[67] Using such designs normally increases the kinetic energy of EGR allowing more of it to flow with lower pumping losses.
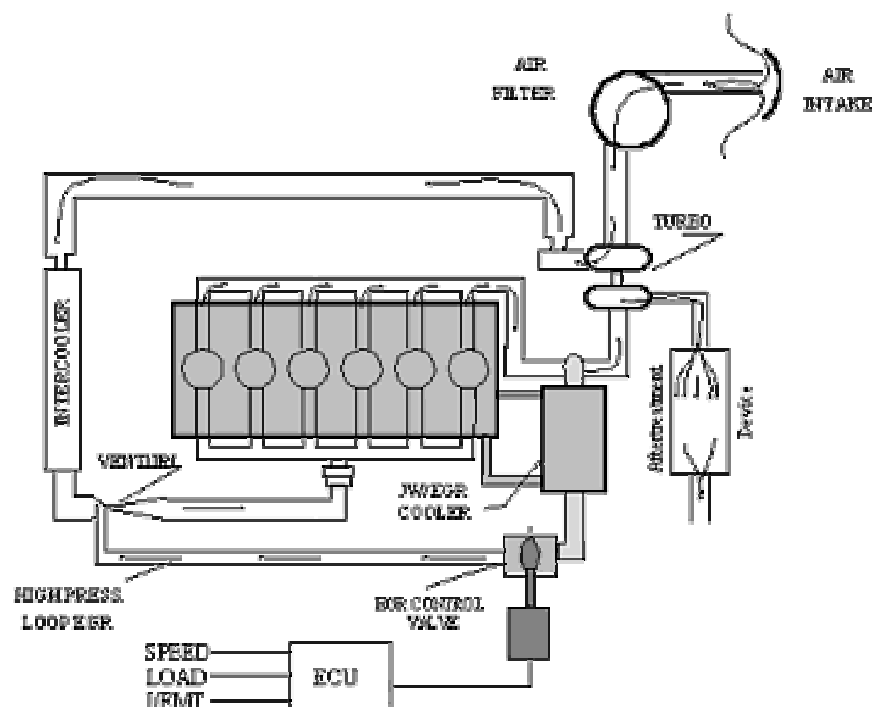
Figure 2- 47. Schematic representation of HPL EGR system with venturi.

Another scheme for EGR implementation in heavy-duty diesel engines is the low pressure loop system (LPL EGR). This system is often employed in conjunction with particulate filter-based aftertreatment systems, where several benefits may accrue. Rather than sourcing EGR from a pre-turbine location (as in the HPL EGR case), LPL EGR systems use exhaust that has been filtered through diesel particulate filters. Figure 2-48 shows a schematic representation of a LPL EGR system where EGR was recirculated from a point downstream from the DPF. This alternate configuration sought to preserve turbocharger performance by supplying exhaust gas from a point downstream of the trap (see Figure 2-48) thus allowing all the exhaust to be utilized in the turbine. At this location, exhaust gas pressure is at a lower level than that of the intake manifold. To promote flow, EGR is introduced back in the engine just upstream of the turbocharger compressor. The pressure difference between points downstream of the trap and upstream of the turbocharger is generally adequate for EGR flow rates needed to reduce US FTP NO_x to the 2.0 g/bhp-hr level, for heavy-duty diesel engines.
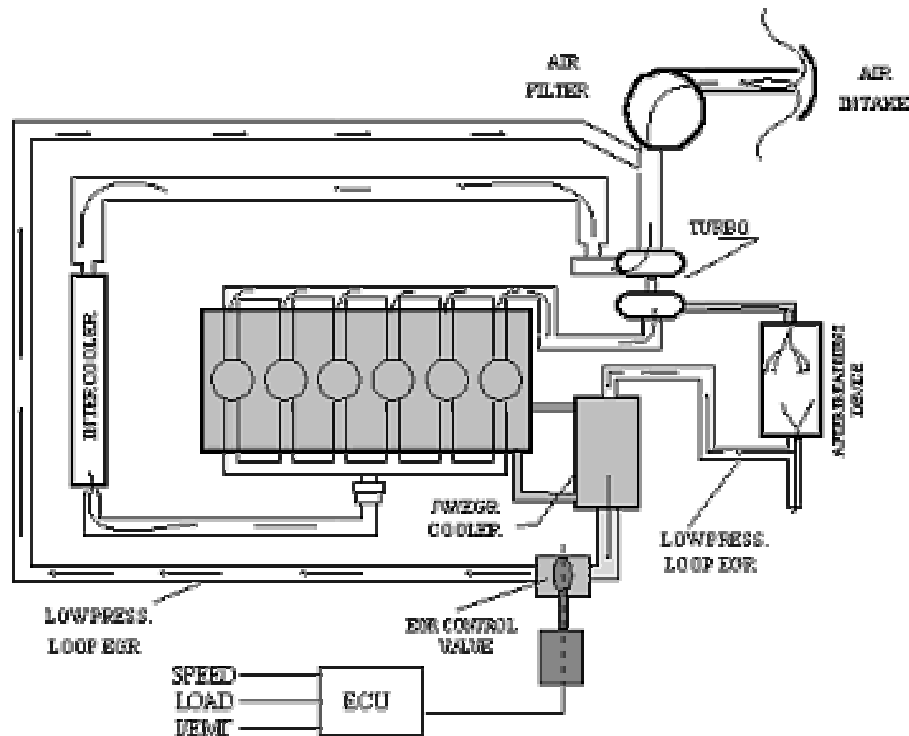
Figure 2-48. Schematic representation of LPL EGR system.

Advantages of the LPL EGR system include:

1) Lower fuel consumption than that of the HPL configuration as a result of better turbocharger performance than that of the HPL configuration. However, if the HPL EGR system is properly executed, the turbocharger would have to be revised to account for the loss of exhaust energy resulting from rerouting some exhaust to the EGR circuit, in which case the HPL configuration should recover its fuel economy loss.

2) With the presence of a particulate filter, the LPL EGR supplies predominantly filtered exhaust to the inlet of the engine through the turbocharger compressor. Therefore, engine durability can be better preserved.

3) Exhaust gas downstream of the particulate filter is cooler than that provided from upstream of the turbocharger (as in the HPL case). Therefore, LPL EGR would have a higher heat absorbing capacity for flow rates similar to those of the HPL EGR.

4) Due to the higher heat absorbing capacity of LPL an opportunity exists to reduce EGR cooling requirements (reduced size EGR cooler) and provide a more compact unit. In addition, the EGR cooler would have less heat rejected in the engine water jacket and therefore, less cooling load for the radiator to handle.

5) Reducing the amount of EGR cooling may help prevent exhaust system condensation and potential erosion of the EGR cooler, EGR valve, EGR piping, and turbocharger compressor wheel.

6) Better EGR and fresh charge air mixing resulting from introducing the mixture upstream of the turbocharger compressor.

With as many advantages as were mentioned, the LPL EGR system has not been favored over the HPL system for a number of reasons described as follows:

1) Even though LPL EGR is sourced downstream from the particulate filter, it is not entirely free from carbonaceous material, since the filter trapping efficiency is less than 100 percent. With carbonaceous material still remaining in the recirculated exhaust stream, its impaction on the compressor wheel as it turns at a high rate of speed may potentially erode the wheel.

2) In cases where air-to-air intercoolers are used, as shown in Figure 2-48, carbonaceous and other unfiltered matter flowing through the compressor would likely be trapped in the narrow cooler passages. If left to accumulate over time, air flow to the engine would be reduced, leading to performance as well as emission and fuel economy deterioration.

3) Unburned oil vapors as well as any unburned fuel adsorbed on the surface of carbonaceous particles accumulating in the inlet system may emit carbon monoxide (CO) gas when exposed to higher temperatures. When this happens, fresh and cooled air to the engine would be displaced by CO that is detrimental to combustion efficiency.

4) Plumbing for the LPL EGR arrangement is often awkward and cumbersome.

C.5.3. Issues Related to EGR Systems

EGR systems would invariably include one or more control valves and one or more EGR coolers. The remainder of the EGR control system consists of piping, flanges and gaskets. With sulfur present in diesel fuel, it is usual to expect sulfur dioxide and sulfuric acid in the exhaust. The same exhaust stream is also laden with soot, unburned oil, unburned fuel, and other trace metals. These exhaust constituents may cause erosion and/or corrosion in the EGR system components, therefore the challenge is to select, design, and develop reliable and trouble-free EGR systems. The following outlines some issues to be addressed when designing these systems.

- **Material Buildup Within EGR Systems:** Carbonaceous material depositing on the walls of the EGR system pipes, coolers, and valves reduces the capacity and efficiency of the system. Carbonaceous deposits restrict EGR flow thus reducing its heat absorbing capacity during combustion, and therefore its ability to reduce NO_x. In addition, these deposits act as insulation, preventing efficient heat transfer from the exhaust gas to the cooling medium. As heat transfer from the exhaust gas

to the cooling medium is reduced, gas temperature proceeding into the combustion chamber tends to rise. This higher temperature reduces the ability of the gas to absorb combustion heat and reduce NO_x emissions.

- **EGR Contaminants:** The presence of sulfur in the EGR system in the form of sulfuric acid must be viewed as a major threat to the integrity of its components. A very important design consideration is the material selection of the EGR cooler. Corrosion in any of the tubes could introduce water (cooling medium) into the engine and perhaps cause a catastrophic failure.

- **Engine Durability:** Introducing unfiltered exhaust gas into the intake manifold, and eventually into the combustion chamber, accelerates deterioration of the cylinder bore and piston rings.[68] The LPL EGR system equipped with a trap has a clear advantage over the HPL EGR in this regard. However, attention must be exercised to avoid water condensation as EGR is introduced upstream of the turbocharger compressor. Extensive testing at various speeds and loads for a given engine should be conducted to determine those regimes that lead to adverse conditions. Cooling EGR may be desirable for NO_x control, but could lead to water condensation that would reduce the turbocharger efficiency and life. Alternative systems that may encompass or enhance EGR filtration should be investigated.

- **Application/Test Cycle:** Effort should be expended in simulating various applications through a carefully designed experiment in a controlled environment. High exhaust gas temperatures coupled with maximum EGR cooling may represent an extreme condition and establish a design target for EGR coolers. However, a large capacity cooler may not be desirable at idle and low loads, especially in extreme cold weather applications. These two extremes present designers with a challenge to optimize the EGR cooler heat transfer capacity or design a cooler bypass, as needed.

- **EGR Cooler Design:** As mentioned earlier, two mechanisms are thought of when explaining the effectiveness of EGR in NO_x reduction. The first mechanism is the dilution of the amount of oxygen which is normally introduced with fresh air. The second mechanism is using EGR as a heat sink. The capacity of the latter aspect is generally proportional to EGR rate, its specific heat, and the temperature differential between EGR and peak combustion temperature. It follows then that the colder the EGR the more effective it would be for NO_x reduction. However, as mentioned earlier, there is a risk of forming condensed water and introducing it into the compressor of the turbocharger. On the other hand, a small EGR cooler capacity may not be as effective in NO_x reduction. The control strategy should be a major determinant for when and how EGR cooling is to be used.

- **EGR System Packaging:** For medium- and heavy-duty diesel engine applications, packaging for durability and long term reliability must be extremely high on the priority list. Several EGR valve design configurations are being considered by suppliers to the diesel OEMs.

- **EGR Valve Control Considerations:** Automotive style EGR valves are mechanical components designed to control EGR flow mainly to achieve emissions reduction. In recent developments associated with medium- and heavy-duty diesel work, more emphasis was placed on EGR control flexibility. For this reason, electronic controls and solenoid actuated EGR valves are fulfilling this need. The proximity of electrical solenoids to hot exhaust has been identified as a potential problem and a limitation for valve performance and durability. Solution to this problem may involve relocating these valves to a cooler environment such as closer to the engine intake manifold. Assessment of the advantages of such a solution should be carried out and design changes proposed and investigated. In addition, integration with engine control algorithms, compensation for performance deterioration over time, and interaction of the EGR system with increased engine back pressure resulting from using certain aftertreatment devices, must be considered.

- **Piping:** Material, size, and route of the EGR system piping will play a significant role in total system heat and efficiency losses. This fact is especially important in the case of the LPL configuration in view of the length of pipe extending from the exhaust side to the inlet of the turbocharger.

While the above is not necessarily a comprehensive list of system design related issues, it does represent a significant selection of the more important concerns that require special attention and effort. The effort is large enough to be supported by various industries and suppliers, such as:

1) EGR valve suppliers

2) EGR cooler suppliers

3) Engine OEMs

4) Exhaust systems suppliers

5) Turbocharger manufacturers

6) Oil companies

C 6. Auxiliary Exhaust Emission Control Devices (Aftertreatment)

In-cylinder design changes and control means for meeting emission standards have been implemented for the last two to three decades. These efforts are approaching the stage of diminishing returns, thus the need for new technologies. Interest in the field of auxiliary emission control devices (AECD) or aftertreatment has been growing. To-date, solutions for NO_x and PM control through catalytic treatment of the exhaust have been found and are being vigorously developed.

C 6.1. Catalytic Solutions

Catalytic solutions for both NO_x and PM reductions have been developed and continue to experience significant success in diesel exhaust emission control applications. The oldest of these systems is the diesel oxidation catalyst that is beneficial in reducing PM. Other forms of oxidation catalysts are being developed for PM reduction. For instance combination of PM filters and oxidation catalysts are finding good success in PM reduction and will be reviewed later in this report. Other catalytic solutions are being developed for NO_x reduction and they are currently receiving the most attention. These catalytic systems for NO_x control include lean NO_x catalysts, selective catalytic reduction, as well as NO_x adsorber systems.

C 6.1.2. Oxidation Catalysts

Diesel oxidation catalysts promote chemical oxidation of CO and HC as well as the SOF portion of diesel particulates. They also oxidize sulfur dioxide that is present in diesel exhaust from the combustion of sulfur containing fuels. The oxidation of SO_2 leads to the generation of sulfate particulates and may significantly increase total particulate emissions despite the decrease of the SOF fraction. Modern diesel oxidation catalysts are designed to be selective, i.e., to obtain a compromise between sufficiently high HC and SOF activity and acceptably low SO_2 activity.

When passed over an oxidation catalyst, a number of exhaust gas components are oxidized by oxygen present in ample quantities in diesel exhaust. The following diesel pollutants can be oxidized to harmless products, and thus can be controlled using the diesel oxidation catalyst (DOC):

- carbon monoxide (CO),

- gas phase hydrocarbons (HC),

- organic fraction of diesel particulates (SOF).

 Additional benefits of the DOC include oxidation of several non-regulated, HC-derived emissions, such as aldehydes or PAHs, as well as reduction or elimination of the odor of diesel exhaust.

The emission reductions in the DOC occur through chemical oxidation of pollutants occurring over the active catalytic sites. Hydrocarbons are oxidized to form carbon dioxide and water vapor. However, an oxidation catalyst will promote oxidation of all compounds of a reducing character; some of the oxidation reactions can produce undesirable products and, in effect, be counterproductive to the catalyst purpose. Oxidation of sulfur dioxide to sulfur trioxide with the subsequent formation of sulfuric acid (H_2SO_4), is perhaps the most important of these processes.

When the exhaust gases are discharged from the tailpipe and mixed with air, either in the environment or in the dilution tunnel that is used for particulate matter sampling, their temperature decreases. Under such conditions, gaseous H_2SO_4 combines with water molecules and nucleates forming (liquid) particles composed of hydrated sulfuric acid. This material,

called sulfate particulates, contributes to the total particulate matter emissions from the engine. Catalytic formation of sulfates, especially in conjunction with high sulfur content diesel fuel, can significantly increase the total PM emissions and, thus, become critical for the catalyst application.

Oxidation of NO to NO_2 is another reaction that may be considered undesirable in some applications. Concerns have been raised that the catalytic generation of NO_2, which is more toxic than NO, can create air quality problems in some underground mine applications.[69] Due to the thermodynamic equilibrium, which is reached in the atmosphere after some time regardless of the original composition of NO_x, the oxidation of NO is probably of less concern in surface applications. Interestingly enough, nitrogen dioxide can be effectively used to facilitate the regeneration of diesel particulate filters. As diesel oxidation catalysts and catalytic particulate filters become more widespread, more research will be needed to clarify the health and environmental effects of increased NO_2 levels that may result from the use of these devices.

The reaction mechanism in diesel oxidation catalysts is explained by the presence of active catalytic sites that are deposited on the surface of the catalyst carrier and have the ability to adsorb oxygen. The catalytic reaction has three stages: (1) oxygen is bonded to a catalytic site, (2) reactants, such as CO and hydrocarbons, diffuse to the surface and react with the bonded oxygen, (3) reaction products, such as CO_2 and water vapor, desorb from the catalytic site and diffuse to the bulk of the exhaust gas.

C.6.1.3. Emissions Performance

Carbon Monoxide and Hydrocarbons: Diesel oxidation catalysts are effective devices to control carbon monoxide and hydrocarbon emissions from diesel engines, including the PAH and hydrocarbon derivatives such as aldehydes. Figure 2-49 illustrates catalyst performance as a function of temperature. The catalyst shows no activity at low exhaust gas temperatures. As the temperature increases, so does the oxidation rate of CO and HC. This is called catalyst "light-off". At high temperatures the catalyst performance stabilizes to form the characteristic plateau on the light-off curve. For most catalyst systems, including the classic Pt/Al_2O_3, the conversion of carbon monoxide is higher than that of hydrocarbons at any given temperature. In a given catalyst there is also a competition between the oxidation of CO and HC species, causing the conversion rates in a mixture of gases, such as in engine exhaust, to be lower than laboratory conversions determined using pure CO gas in the absence of HC, or vice versa.
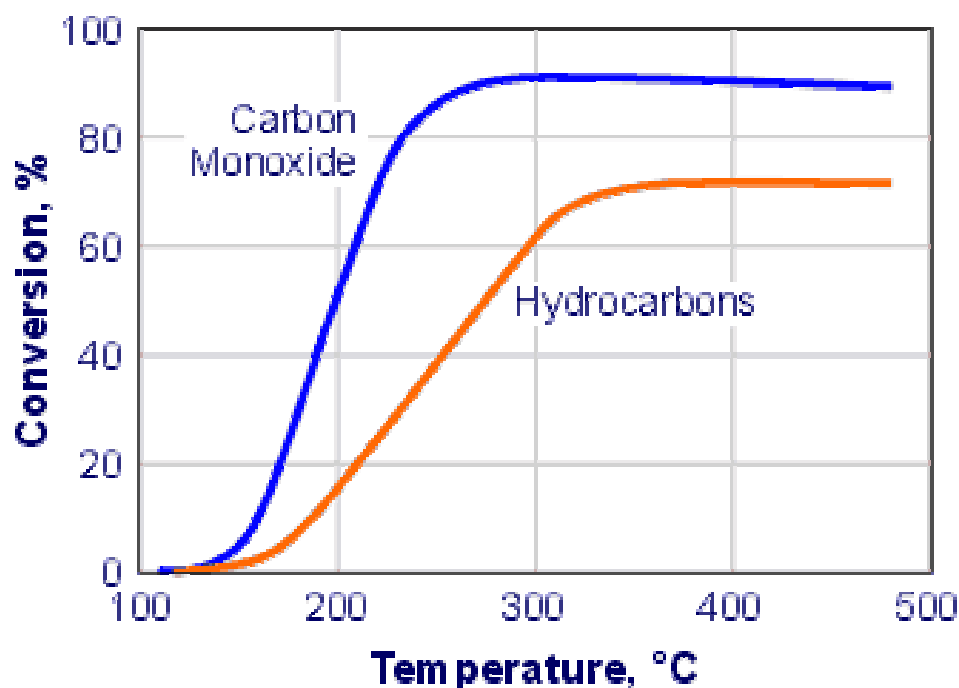
Figure 2-49. Conversion of CO and HC in diesel oxidation catalysts.

The high temperature conversion rate for CO or HC, or the height of the plateau, depends on the mass transfer conditions in the catalyst. Consequently, it can be increased or decreased by changing factors that affect either the mass transfer coefficient or the mass transfer surface area. For example, the maximum conversion of CO or HC will increase when a larger catalyst or a higher cell density substrate is used. In fact, the high temperature conversion efficiency can be brought as close to 100 percent as desired by enlarging the catalyst size. If needed, the conversion efficiency can be limited by using a smaller catalyst, or one of a lower cell density (larger cells).

The light-off temperature, on the other hand, depends mainly on the chemical reaction kinetics in the catalyst. Therefore, it is influenced primarily by the catalyst noble metal/washcoat system. The overall performance of a catalyst system, as measured on standard emission test cycles, is, thus, a combined result of the applied catalyst technology and the substrate geometry. Among the two common oxidation catalysts—platinum and palladium—platinum (Pt) is most active for the oxidation of CO and HC in diesel exhaust, as illustrated in Figure 2-50.[70] The applied catalysts used 400 cpsi substrates of 5.07 liter volume. CO emissions with the Pt catalyst were less than a half of those with the palladium (Pd) catalyst. Also the hydrocarbon emissions were lower when the platinum catalyst was used, although the performance difference between Pt and Pd was smaller.
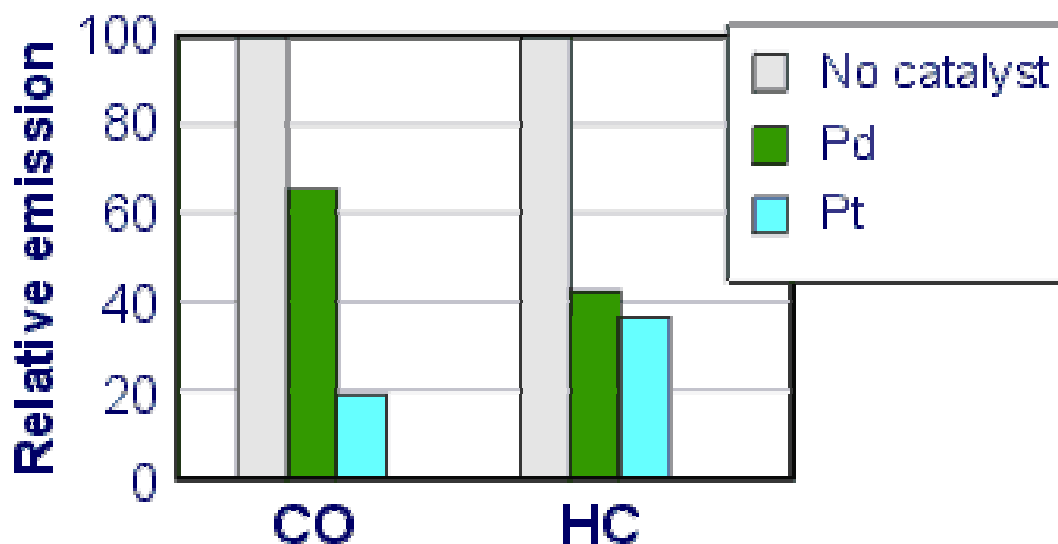
Figure 2-50. Platinum and palladium diesel oxidation catalyst performance.
(6.925 liter DI turbocharged aftercooled diesel engine, HD FTP Transient test).

The lower activity of Pd in diesel exhaust—widely confirmed in the literature—is quite opposite to its activity in gasoline exhaust.[71,72] Palladium, due to superior low temperature hydrocarbon activity, is commonly used in close-coupled light-off catalysts in gasoline cars.[73] The difference in activity is explained by different chemical composition of gasoline and diesel exhaust hydrocarbons. Gasoline HCs have short carbon chains and contain many unsaturated compounds, while diesel hydrocarbons are characterized by long carbon chains and mostly saturated bonds.

Observed heat effects associated with the oxidation of carbon monoxide and hydrocarbons are different in the gasoline and diesel oxidation catalyst. The oxidation of CO and HC involves exothermic reactions with significant release of heat. Of course, the heats of reaction for particular chemical compounds are identical whether they originate from diesel or gasoline exhaust. The difference is in the concentrations of CO and HC that are many times higher in gasoline exhaust than in diesel exhaust. As a result, a temperature increase of a few hundred degrees Celsius is not uncommon in the gasoline catalytic converter while the temperature rise across the diesel catalyst is rarely more than 10-20°C.

The total diesel particulate matter (TPM) emission is composed of three major fractions including the carbonaceous particulates, the organic particulates (SOF), and sulfates (SO_4). Each of these fractions behaves differently over the diesel oxidation catalyst. In general, the overall effect of the DOC on the total PM emission could be a decrease, as well as an increase. Typical transformations of the three fractions and the resulting total PM emissions are schematically illustrated in Figure 2-51. As apparent from the graph, PM emissions can be reduced in the DOC through the removal of their organic fraction (SOF). Under certain conditions, however, the SOF decrease can be more than off-set by an increase of sulfate PM, leading to an overall increase in TPM emission (if high sulfur fuels are used, sulfate particulate emissions may be much higher than shown in Figure 2-51).
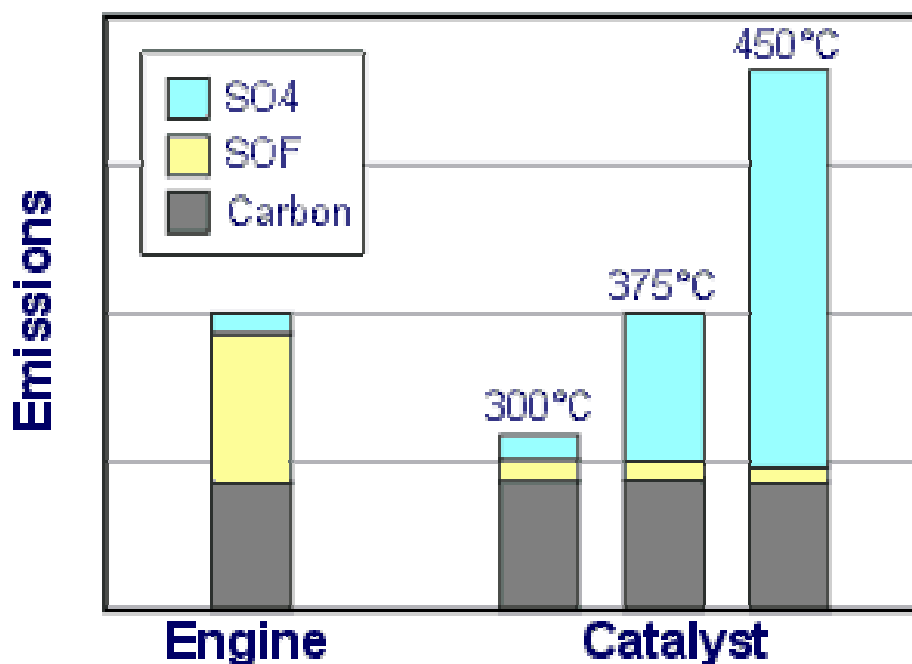
Figure 2-51. Impact of diesel oxidation catalyst on PM emissions.

While literature reports exist that show both small decreases and small increases of solid, insoluble PM in the DOC, it is generally agreed that carbonaceous particulates pass virtually unchanged through oxidation catalysts.[73] Considering their large size in comparison to gas molecules, carbon particles are not likely to come into contact with the catalyst. Even if they do, both the residence time and the temperature in diesel exhaust are insufficient for any significant oxidation rates. Any carbon oxidation that may occur is likely attributed to NO_2,[74] which is active at lower temperatures than oxygen. Catalyst substrates that increase residence time by impinging carbon particulates onto a porous metal layer, to allow for the oxidation by nitrogen dioxide to take place[75] have been under development. Reports on changes in PM carbon fraction over DOCs must be always approached with careful scrutiny. The magnitudes of change in many of such reports are on the threshold of detection. Measurement error can be magnified due to the analytical methods that determine insolubles only indirectly, by subtracting sulfate and SOF from total PM. If sulfuric acid reacts with metals, such as with calcium from lube oil additives, the resulting sulfate salts may be accounted for as insoluble material.

The organic fraction (SOF) of diesel particulates, composed of heavy hydrocarbons of high boiling temperatures, is very effectively oxidized in the catalyst. SOF removal is the major effect contributing to a decrease in the TPM emissions over the diesel oxidation catalyst. SOF oxidation is similar to the oxidation of gas phase hydrocarbons, i.e., a certain temperature has to be reached for the catalyst to light-off (Figure 2-51). After the light-off temperature is reached, the conversion of SOF shows little change with further temperature increase.

The sulfate fraction of diesel particulates (SO_4) is increased in the DOC due to the oxidation of SO_2 with subsequent formation of sulfuric acid. This process is counter-productive and causes

an increase in TPM emissions. The intensity of the sulfate make increases with exhaust gas temperature and becomes critical at about 400°C. Special catalyst formulations are used to suppress that process and, thus, to make the diesel oxidation catalyst a viable PM reduction approach. Low sulfur fuels minimize sulfate make and allow the use of more active diesel oxidation catalyst formulations.

The net effect of the DOC on diesel particulate matter is a combination of the SOF and SO$_4$ reactivities, as it was shown in Figure 2-4 (for the sake of simplicity, the dependence of engine-out PM composition on exhaust temperature has been neglected). The catalytic oxidation of SOF contributes to the decrease in TPM while the generation of sulfates increases particulate emissions. The desired SOF effect prevails at low temperatures. In practice, if sulfur is present in the fuel, there is always a temperature above which an increase of PM emissions will be recorded. Selective catalysts are formulated to suppress the sulfate generation in order to extend the catalyst PM control function into higher exhaust temperatures. Considerable amount of catalyst research produced diesel catalysts specifically optimized for particulate matter control that can tolerate certain sulfur levels in the fuel and still control PM emissions. These selective formulations, however, compromise the catalyst activity, resulting in less effective gas phase HC and CO control. If sulfur-free fuel is used, the conventional highly active platinum/alumina based catalysts may be still the best choice for both the particulate and the gas phase emission control.

PM Emission Reduction: The potential of catalytic PM emission reduction critically depends on the composition of engine-out particulates. Only particulates of high SOF contents, so called "wet" particulates, can be effectively controlled by catalysts. In practice, different engine manufactures design the combustion in different ways to meet emission standards. As a result, the PM portion that is susceptible to oxidation varies from engine to engine. In a system approach to the design of the engine-catalyst package, particulates can be purposely made "wet" by engine design measures to allow for more efficient catalytic control. In a given engine, SOF content depends on the operating conditions, changing widely from just about a few percent at high engine loads to well above 50 percent at low loads. The average SOF content over an engine test cycle depends on its average load factor. Cold test cycles of low engine loads will produce wet particulates, which can be effectively controlled by the DOC (as long as the temperatures are sufficient for the catalyst to light-off). Hot, highly loaded test cycles, on the other hand, tend to produce dry particulates, which can be controlled to a little degree by the DOC technology.

Wet particulates—collected over lightly loaded test cycles—can have SOF contents of more than 50 percent. Since the SOF fraction can be effectively removed by the catalyst, the potential for catalytic particulate control in such cases can be quite significant. In practice, PM reductions are additionally limited by the sulfur level in the fuel and by the catalyst temperature. Advanced catalyst formulations, in conjunction with low sulfur fuels, can be very effective in controlling particulates from low temperature applications. PM removal efficiencies of 50 percent and more have been recorded with diesel cars tested on the relatively cold ECE+EUDC cycle using fuels of less than 500 ppm sulfur.[76] In heavy duty applications using the same 500 ppm sulfur fuel, the PM emission reduction potential is in most cases limited to 20-30 percent.

In the US EPA Urban Bus Retrofit Rebuild (UBRR) program, a number of catalysts were certified to achieve a 25 percent PM emission reduction over the (medium load) FTP transient cycle on two-stroke engines. Most of these catalysts were not able to achieve the same 25 percent PM emission reduction on four stroke engines, which produce PM emission of lower SOF content than the two-stroke technology. Even when tested on rather cold test cycles, such as the Japanese 13-mode, PM emission from heavy-duty engines could be reduced by only about 20 percent, due to high sulfate production during the high temperature modes.[77] It could be reasonably expected that higher PM emission reductions would be possible with ultra low sulfur diesel fuels. On the other hand, the oxidation catalyst technology has not been successful in controlling diesel particulates from very hot applications and test cycles, such as the European R-49, ESC, or ETC.

Finally, it should remembered that diesel particulates are sometimes defined in different ways, which may have implications for catalytic control technologies. In some occupational health regulations, diesel particulates are determined as elemental carbon (EC). In such case, the DOC technology would be ineffective in controlling PM emissions. In certain other regulations, diesel particulates are defined as total carbon (TC), i.e., including the SOF part, but excluding sulfates. In this case, catalysts can be a very effective control approach, as the sulfate make is no longer an issue.

Polynuclear Aromatic Hydrocarbons: PAH emissions are divided between the gas and particulate phases. The heaviest PAHs constitute part of the SOF fraction of diesel particulates, while the lighter species can be identified as part of the gas phase HC emission. The HC and SOF effectiveness of the diesel oxidation catalysts extends on the PAH class of compounds and other HC derivatives. Table 2-10 lists PAH results from two DOCs tested on a heavy-duty diesel engine at SwRI (test cycle: FTP Transient; engine: 1998 model 12.7 liter DDC series 60 EUI engine, turbocharged and aftercooled, rated 400 hp @ 1800 rpm). The two catalysts provided average PAH emission reductions of 68 and 54 percent, respectively.[78]

Table 2-10. Catalytic conversion of PAH emissions.

Compound	Baseline	Cat B	Cat D	Red Cat B	Red Cat D
	µg/bhp-hr	µg/bhp-hr	µg/bhp-hr	%	%
Napthalene	295	159	182	46.1%	38.3%
2-Methylnapthalene	635	278	277	56.2%	56.4%
Acenapthalene	40	13	13.6	67.5%	66.0%
Acenapthene	46	25	24.4	45.7%	47.0%
Fluorene	72	29	28.9	59.7%	59.9%
Phenanthrene	169	54	56	68.0%	66.9%
Anthracene	10	2.6	2.8	74.0%	72.0%
Fluoranthene	7.7	2.6	4.9	66.2%	36.4%
Pyrene	14	5	6.4	64.3%	54.3%
Benzo(a)anthracene	0.22	0.05	0.18	77.3%	18.2%
Chrysene	0.51	0.16	0.33	68.6%	35.3%
Benzo(b)fluoranthene	0.26	0.09	0.12	65.4%	53.8%
Benzo(k)fluoranthene	0.15	0.05	0.08	66.7%	46.7%
Benzo(e)pyrene	0.26	0.08	0.14	69.2%	46.2%
Perylene	0.01	0	0	100.0%	100.0%
Indeno(123-cd)pyrene	0.13	0.04	0.07	69.2%	46.2%

Compound	Baseline	Cat B	Cat D	Red Cat B	Red Cat D
	µg/bhp-hr	µg/bhp-hr	µg/bhp-hr	%	%
Dibenz(ah)anthracene	0.01	0	0	100.0%	100.0%
Benzo(ghi)perylene	0.32	0.1	0.22	68.8%	31.3%
Total	1290.57	568.77	597.14	55.9%	53.7%
Average Reduction				68.5%	54.1%

Sulfate Formation: Catalyst selectivity was the focus in the development of the diesel oxidation catalyst through the 1990's. A selective catalyst would exhibit high activity towards the oxidation of hydrocarbons but, at the same time, low activity in the oxidation of sulfur dioxide and low sulfate particulate make. A lot of research has been conducted to understand the mechanisms of catalytic sulfate formation on different catalyst systems and with fuels of different sulfur contents. A number of commercial catalysts have been developed for the 500 ppm S fuel which represents the certification fuel in the USA (1994), Europe (1996), and Japan (1996). Lower sulfur levels always yield better PM control, especially at higher temperatures. The selectivity of diesel catalysts and the sulfate emission problem will likely become less important in the future, when ultra low sulfur diesel fuels of 10-15 ppm sulfur are commonly used.

The generation of sulfates in the diesel oxidation catalyst depends on the following factors:

- Sulfur content in the fuel

- Catalyst temperature

- Catalyst formulation.

Sulfur dioxide, the precursor of sulfate particulates, originates from the fuel sulfur. The lower the content of sulfur in the fuel, the less SO_2 is present in the exhaust gas, and the less sulfates are generated in the catalyst. A very illustrative experimental results on the dependence of sulfate formation on the fuel quality are shown in Figure 2-52,[79] which compares the total particulate matter emissions with a platinum-based non-selective oxidation catalyst for three different diesel fuels containing 1500 ppm, 500 ppm, and 25 ppm of sulfur. For the sake of clarity, the composition of PM (carbon, sulfate, SOF) is not shown in the graph. The particulates are composed mostly of SOF at the lowest, 130°C, temperature. At higher temperatures, the particulates are composed primarily of sulfates. The carbon fraction is not more than 0.01 g/kWh at any catalyst temperature.
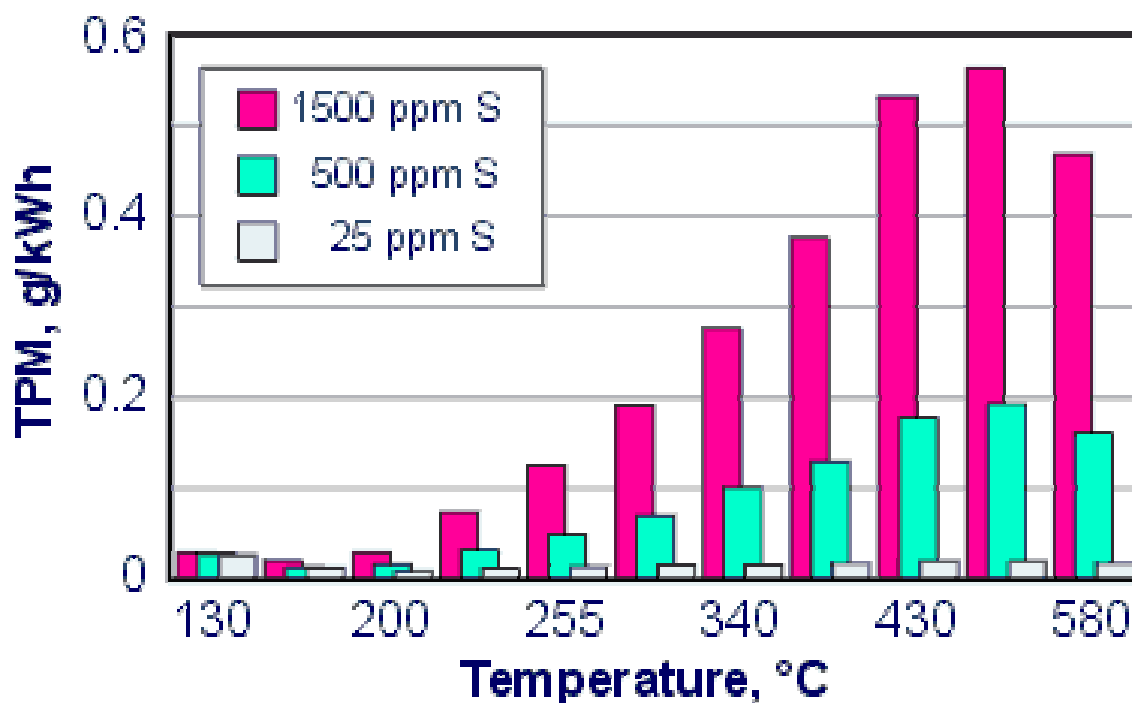
Figure 2-52. Effect of fuel sulfur on particulate emissions when using a doc.

A substantial increase in the TPM emissions was observed with the 1500 ppm sulfur fuel. Obviously, the non-selective catalyst is totally inappropriate for this application. Also the 500 ppm sulfur fuel, known as the "low sulfur fuel", still contributed to a significant sulfate generation. When used with the 500 ppm sulfur fuel, the non-selective catalyst can still increase the engine out PM emissions several times, especially at higher temperatures, due to the sulfate generation. Only with the 25 ppm sulfur fuel the catalyst sulfate make was almost insignificant over the entire temperature range. Hence, a non-selective oxidation catalyst can be used only in conjunction with fuels of very low sulfur levels (or with a sulfur free fuel), without increasing the PM emissions.

C 6.1.3. Lean NO_x Catalysts

Two groups of catalyst systems are known for the reduction of NO_x with hydrocarbons: a copper substituted zeolite ZSM5 catalyst, which is active at high temperatures, and a platinum/alumina catalyst, exhibiting low temperature activity. Both catalysts have narrow operating temperature windows, resulting in only a limited NO_x reduction efficiency, and exhibit other problems. Some lean NO_x catalysts have been commercialized, primarily to provide small deNO$_x$ functionality in diesel oxidation catalysts.

After it became apparent that NO decomposition catalysts had too many shortcomings to produce a robust, commercial catalyst system,[80] research turned towards selective reduction of NO_x by compounds of combustion gases. It was discovered that several catalysts promoted selective catalytic reduction of NO_x by hydrocarbons or other exhaust gas components (carbon monoxide, alcohols, …).[81] Catalysts selectively promoting the reduction of NO_x by hydrocarbons have been termed "lean NO_x catalysts" (LNC) or "deNOx catalysts".

NO$_x$ reduction by HC was found to be less susceptible to sulfur poisoning than NO decomposition and higher conversion efficiencies were demonstrated. In the case of the diesel application, diesel fuel was the obvious source of hydrocarbons necessary for the reaction. Since the enrichment of exhaust gases with diesel fuel seemed more straightforward than carrying on-vehicle ammonia vessels, catalyst research focused on that process and produced numerous technical publications. In fact, selective NO$_x$ reduction by hydrocarbons became the mainstream in NO$_x$ reduction catalyst research over the period of early- to mid-1990's.

In the selective catalytic reduction, hydrocarbons react with NO$_x$, rather than with O$_2$, to form nitrogen, CO$_2$, and water. LNCs have to be optimized to selectively promote the desired reaction with hydrocarbons over the undesired reaction with oxygen. The catalyst selectivity is determined by the catalyst formulation, but it also depends on a number of other factors, such as the hydrocarbon species used for the reaction, the temperature, the exhaust gas oxygen content, and the HC/NO$_x$ ratio.

Passive and Active LNC: The most attractive source of hydrocarbons for reducing NO$_x$ is the diesel exhaust itself. Systems utilizing exclusively the native diesel HCs are referred to as the "*passive LNC*" catalysts.

Passive systems, thanks to their simplicity, reliability, and lower cost, are always the preferred emission control option. However, due to the selective character of the reaction, LNCs show increasing NO$_x$ conversion rates with increasing hydrocarbon concentrations. The limited supply of native diesel hydrocarbons (which is actually quite low in comparison to the NO$_x$ emission levels) may constitute a barrier in achieving higher NO$_x$ conversions, especially if the catalyst selectivity is low. Enrichment of the exhaust gases with additional HC material has been perceived as a solution to this problem. In general, such enrichment could be realized by two methods:

- Injection of hydrocarbons, preferably diesel fuel, into the exhaust system upstream of the catalyst, or

- Late in-cylinder injection in a common rail fuel system (or merely late injection timing in conventional fuel systems).

Catalysts with HC enrichment have been termed "*active LNC*" systems. The concept of passive and active LNCs is illustrated in Figure 2-53.
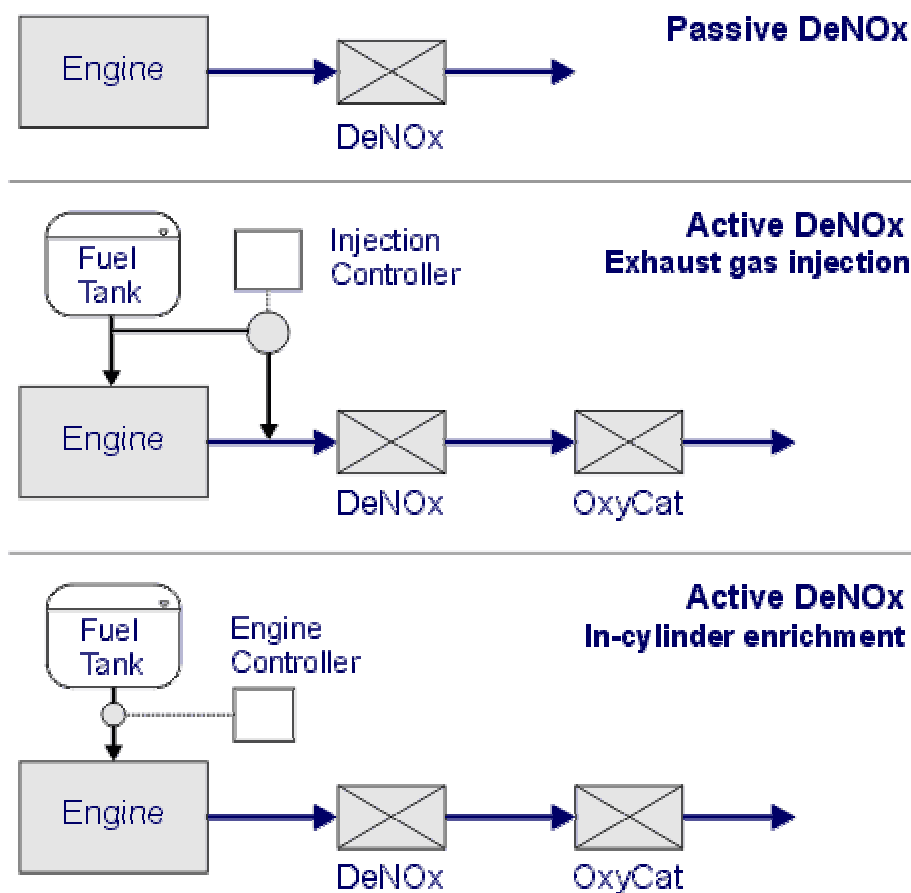
Figure 2-53. LNC (DENO$_X$) configurations.

Systems for injecting hydrocarbons into the exhaust gas can be designed to reliably provide the required quantity of hydrocarbons to the LNC. They are, however, quite complex and, thus, costly. By using common rail post-injection, the cost of implementation of an active system can be fairly low. The biggest problem, especially in view of the continuous character of fuel enrichment that is required, is cylinder wall wetting by the fuel spray and its impact on the lube oil film and engine wear.[82] The application of simple late injection timing, which would have a less detrimental effect on engine durability, was reported to be less effective due to the propensity of hydrocarbons for partial combustion/cracking before reaching the catalyst.[83] Both types of HC enrichment also involve a certain fuel economy penalty, which depends on the quantity of injected fuel. An additional oxidation catalyst may be necessary in the active configurations to oxidize hydrocarbons that may pass through the LNC.

Types of LNCs: Numerous catalyst systems, both precious and base metal based, were reported to exhibit lean NO$_x$ reduction activity. Some of these formulations, grouped by washcoat technology, are listed in Table 2-11.[84]

Table 2-11. Lean NOx catalyst systems.

Washcoat	Metal
Zeolite-based (mainly ZSM5)	Cu, Pt, Mn, Fe, Co, Ni, Zn, Ag, Ce, Ga
Alumina-based	Pt, Pd, Rh, Ir, Ru, Pt-Rh, Pt-W, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag
Silica-alumina	Co, Cu
Titania, sulfated titania	
Zirconia, sulfated zirconia	

Some very optimistic results that were published made an encouraging impression that the problem was almost solved. In reality, the multitude of systems under development proved that the catalysts were far from being perfect. Some of the reported laboratory conversion efficiencies and their corresponding temperatures are listed in Table 2-12.

Table 2-12. Reported laboratory LNC performance.

Catalyst	Peak NO_x Conv. (%)	Temperature (°C)	Reducing Agent
Cu/ZSM5	60	400	C_2H_4
H-Mordenite	62	400	C_3H_8
Ga-Ferrite	100	600	C_3H_8
Ga/ZSM5	100	500	C_2H_6
SnO_2	67	400	C_2H_4
Ag/Al_2O_3	80	400	C_3H_6

Most of these catalyst systems were eventually disqualified as LNC candidates. Eventually, a consensus had been reached that the following two groups of catalyst showed the most promise for further development:

- Copper exchanged zeolite **Cu/ZSM5**, and

- Platinum on alumina **Pt/Al₂O₃**.

Each of these catalysts exhibits a maximum NO_x conversion at a certain exhaust temperature. The Cu/ZSM5 is active at high temperatures, between 350 and 500°C, while platinum catalysts are active at lower temperatures, approximately 200-300°C. Their maximum NO_x conversions measured in laboratory reactors typically amounts to 50-60 percent, as illustrated in Figure 2-54. The combined Pt/Al₂O₃ and Cu/ZSM5 curves reflect the maximum NO_x reduction potential of that technology. It should be emphasized that the presented performance is typical for lean exhaust gas condition of high O₂ concentration (say, 5-10 percent), as is the case in diesel exhaust. Lean NO_x catalysts can perform significantly better with low oxygen content (see Figure 2-54 and the following discussion).
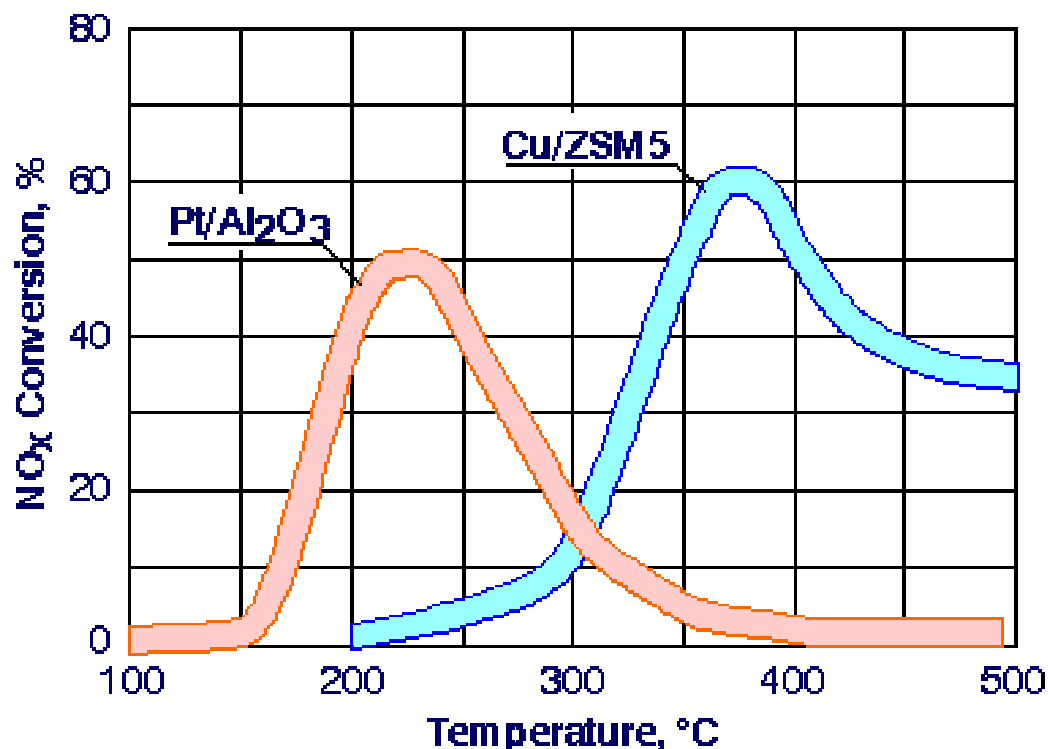
Figure 2-54. Types and performance of LNCS.
(Typical laboratory performance, HC1/NOx ~ 6-12).

There is no single catalyst that would be able to cover the entire temperature range. This is a more serious limitation of the technology than it appears to be, because the operating temperature windows for the platinum and zeolite catalysts do not match the desired temperature range for most diesel engines. In many diesel engine applications, a significant portion of NO_x emissions can be generated at temperatures between 250 and 350°C, which is exactly in the area between the capabilities of the platinum and zeolite catalysts.

Both catalyst systems work most effectively using hydrocarbons as the reducing agent. Carbon monoxide or hydrogen are not effective reductants. The maximum selectivity of these catalysts is only about 20 percent, i.e., 20 percent of HC reacts with NO_x and 80 percent with oxygen. Thus, relatively large amounts of HC are necessary for the reduction of NO_x. HC1 to NO_x ratios between 3 and 12 were usually used in laboratory evaluations, with higher ratios resulting in better catalyst performance, while the ratio of HC to NO_x in native diesel exhaust is typically below 1. Therefore, higher NO_x conversions can be achieved in active LNC systems, which feature exhaust gas hydrocarbon enrichment. In most diesel applications, even the performance of a 100 percent selective catalyst could be improved by hydrocarbon injection. If fuel were injected, injection rates of approximately 3 percent of the engine fuel consumption would be necessary to achieve HC1 to NO_x ratios greater than 3.[84]

Issues With Advanced Catalyst Systems: LNCs as discussed above, have never been developed to provide the high levels of NO_x reduction required by future emission standards. The major unsolved problems could be summarized as follows:

1) Catalysts require some form of HC enrichment; HC levels in diesel exhaust, especially in modern engines, are too low for any significant NO_x reduction using passive LNCs.

2) Even with HC enrichment, the maximum conversion efficiency at realistic HC/NO_x ratios is low (30 percent or less).

3) Temperature window of known catalysts is narrow and not always corresponds to the exhaust gas temperature range, at which most NO_x is emitted from the engine.

4) Catalyst durability needs to be improved - both resistance to poisons and, in the case of Cu/ZSM5, thermal durability.

5) Catalysts need to be more selective towards reducing NO_x to nitrogen, as opposed to nitrous oxide.

Solutions to these problems can be classified into two groups: (1) optimization of catalyst formulation and (2) optimization of the emission control system. Better catalysts could provide such benefits as improved efficiencies, wider temperature window, or, last but not least, better durability. Even in the absence of new, breakthrough catalyst formulations, significant improvement can be achieved by system optimization. Reported ideas include using two catalysts, possibly of different formulations, optimized catalyst locations (close-coupled, underfloor), optimized HC enrichment strategies (including exhaust flow by-passes), exhaust gas cooling, and more.

A multitude of studies, especially over the 1990's, focused on improving the performance of LNCs. The following sections provide a brief overview of selected LNC research. The selection of discussed studies is by no means complete. However, considering the limited degree of LNCs commercialization and the only moderate future potential, we hope that a sufficient insight into the various directions of LNC research is provided.

Catalyst Chemistry Optimization: One approach to address the drawbacks of the "classic" LNCs is to combine different catalyst technologies together. In particular, there have been numerous attempts to extend the catalyst window by designing complex catalysts that would incorporate a number of catalytic components, which would be active at different temperature ranges (e.g., to combine both ZSM5 and Pt catalysts or their modifications together). An example of such formulation combines three components. A first catalytic component, cobalt (Co) on δ-alumina washcoat, is active at high exhaust temperatures. A second component, Pt/Rh/Co alloy dispersed on BaO-stabilized δ-alumina, provides medium temperature activity. Finally, a third component, Pt/Rh on δ-alumina, is active at low temperature. These three components may be placed in the exhaust system as three separate catalysts, arranged in sequence, or may be coated on a single substrate as three catalyst layers (in this configuration, the third component forms the first catalyst layer, i.e., is deposited on the substrate first). The NO_x reduction activity of this catalyst was claimed to span over the 200 - 800°C temperature range.

Combined catalyst systems have been also developed to enhance the CO utilization in the LNC catalyst. In other words, catalyst systems were optimized to facilitate selective reduction of

NOx not only by hydrocarbons, but also by carbon monoxide. A two-stage catalyst system proposed to achieve this objective included an upstream Cu/ZSM5 catalyst operating through reactions with hydrocarbons, and a downstream Au-Pt/TiO$_2$ catalyst, which enhanced the reactions with CO. That catalyst system was also reported to provide enhanced sulfur poisoning resistance.

Iridium Catalyst: Iridium was first used as a lean NOx catalyst in combination with platinum. A two layer catalyst, combining (1) Pt/Ir on -alumina/ceria with (2) Cu/Fe mordenite, was reported to show higher temperature activity and a wider temperature window relative to the base Pt/Al$_2$O$_3$ formulation.[86]

System Optimization: An important area of LNC system optimization is related to widening the catalyst temperature window. By splitting the catalyst into two and placing them at different locations, one can extend the LNC temperature range. In light-duty application, the first catalyst would be placed in the close-coupled position, exposed to higher temperatures, while the second catalyst would be in the colder, underfloor position. This concept was developed by Daimler and Degussa for a light-duty diesel vehicle.[82] An interesting internal exhaust gas bypass was designed to prevent depleting the gas from hydrocarbons in the upstream catalyst. The bypass involved leaving the perimeter of the front, close-coupled LNC catalyst substrate uncoated. A portion of the exhaust that passed through these uncoated channels provided a source of HC for the downstream (underfloor) LNC. Because of the differences in temperature of the two converters, the effective operating window of the LNC system was broadened. An active LNC catalyst system using this internal bypass concept and in-cylinder HC enrichment was commercialized over a brief period of time on C-Class Mercedes cars.

Further widening of the temperature window, in particular over the European ECE+EUDC cycle, is possible through introduction of exhaust gas cooling during hot driving segments. [87] The system shown in Figure 2-55 was proposed based on a comprehensive optimization study involving different catalyst formulations, configurations, and HC injection strategies on both light- and heavy-duty engines.[88] For light-duty applications, NOx reductions up to 36 percent over the ECE+EUDC cycle were measured when using a heat exchanger and HC injection in front of each of the two catalysts. For heavy-duty applications (ESC test cycle), NOx reduction of about 20 percent was measured at a 3 percent fuel economy penalty, and about 40 percent at a 9 percent fuel economy penalty.
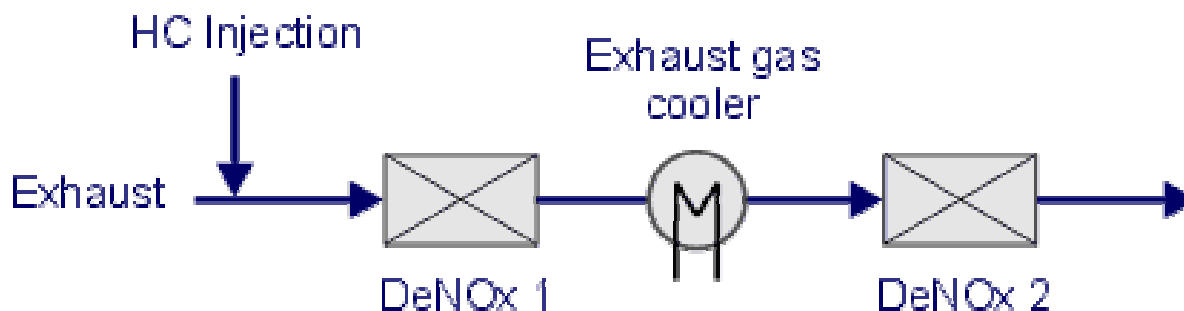
Figure 2-55. Two-LNC system schematic.
(DeNOx 1 - close coupled with bypass; DeNOx 2 – underfloor).

The system in Figure 2-55, proposed for light duty vehicles, includes two LNCs each of them having a volume of 0.8 - 1.2 of the engine displacement. The first catalyst, installed in the close-coupled position, includes a bypass. A heat exchanger in front of the second, underfloor catalyst cools the exhaust gas to between 200-280°C at the catalyst inlet. The first catalyst reduces NO_x during the ECE part of the European driving cycle, while the second catalyst is active during the hotter, EUDC part of the cycle.

Demonstration Programs: Several LNC formulations (ICT - Degussa), including precious metal and base metal (Cu/ZSM5) catalysts, were tested at SwRI on a Caterpillar 3116, 6.6 liter, 4 cylinder, intercooled and turbocharged diesel engine.[89] Emission tests were measured under steady-state conditions as well as on the US FTP transient cycle. Diesel fuel was sprayed into the exhaust stream as a source of secondary hydrocarbons. Diesel fuel of 0.03 percent by weight sulfur, a cetane number of 45.2 and 35 percent aromatics was used for the tests. Steady- state tests were conducted at 1400 rpm. The catalyst size was 5.66" diameter x 6.0", resulting in a space velocity of 55,000 1/hr. Secondary fuel was injected to the catalyst at a rate of 3 percent of the engine fuel consumption. It was found that precious metal catalysts could reduce NO_x but greatly increased PM emissions due to the generation of sulfate particulates. On the other hand, the base metal catalysts of high light-off temperature were not able to oxidize the added secondary fuel at low temperatures and, as a result, increased CO and HC emissions.

A larger catalyst size utilizing two round substrates 7.5" x 7" each was tested on the FTP cycle with optimized fuel injection patterns. The best combined NO_x/PM results were achieved using a base metal catalyst and 3 percent secondary fuel injection. A simultaneous 12 percent NO_x and 25 percent PM reduction was demonstrated.

Another engine dynamometer evaluation was performed on the same Caterpillar 3116 engine model.[90] Nine "black box" catalysts supplied by different manufacturers were tested at steady-state and transient conditions. The space velocities during the steady state tests varied between 10,000 and 40,000 1/hr. Catalyst volumes from 7 to 28 liters were used for the US FTP transient test evaluations. Diesel fuel or ethanol was used as a supplemental reductant. NO_x reductions from 17 to 44 percent were seen during the steady-state tests. However, due to the narrow catalyst temperature windows, much lower NO_x conversions were recorded on the transient test. Several of the transient tests produced marginal NO_x improvements of not more than 5 percent. The best FTP cycle NO_x reduction, achieved using a 28 liter catalyst, amounted to 24 percent but it was accompanied by a 26 percent increase in PM emission.

The best NO_x performance was observed when the HC1/NO_x ratio was higher than 6. It was also found that, depending on the tested catalyst, 35 to 75 percent of NO_x was converted to N_2O rather than to nitrogen. A linear correlation was found between the generation of N_2O and reduction of NO_x.

Commercial Status: Unless more selective catalysts are found, the lean NO_x technology represents only small to moderate NO_x reduction potential. Even though peak NO_x reductions measured in laboratories are frequently in excess of 60 percent, performance of these catalysts over regulatory test cycles is usually limited to 10-20 percent, due to the following reasons:

1) Temperature windows of LNCs tend to be narrow and not always correlate well with the temperatures seen in real duty operation or over the regulatory emission test cycles.

2) Passive systems are further limited by insufficient hydrocarbon supply in the native diesel exhaust.

Other LNC issues include durability and sulfur tolerance concerns, as well as secondary emissions. Since most LNCs that have been commercialized are based on the platinum formulation, it can be reasonably conjectured that a significant portion of NO_x is reduced to nitrous oxide (N_2O), rather than to N_2, over these devices. Since N_2O is not a regulated emission, it is not currently measured during certification testing (no data is published by the catalyst manufacturers). However, despite its unregulated status, N_2O is not a desired product of catalytic reactions.

For all these reasons, commercial LNC applications take usually the form of a small, passive NO_x reduction functionality incorporated into other technologies, primarily into diesel oxidation catalysts. Iridium based catalysts in the passive configuration, discussed above, were introduced by Degussa to some models of diesel fueled cars in Europe in the mid-1990's as (probably) the first commercial lean NO_x catalyst application.

Since the late 1990's, a number of diesel car models in the EU is using Pt-based oxidation catalysts incorporating zeolite HC traps and optimized for passive LNC activity. In one EURO III application, the overall NO_x emission reduction of such a catalyst over the ECE+EUDC cycle, as reported by ASEC, amounted to 19 percent.[91] A Pt-based LNC was a part of the "QuadCAT" kit that was being developed by California-based Ceryx Inc. for retrofitting heavy-duty diesel engines.[92] The QuadCAT electronic control unit could be programmed to deliver different amounts of diesel fuel upstream of the LNC, to serve as hydrocarbon enrichment. NO_x reductions were reported to be strongly dependent on the amount of supplementary diesel fuel added. For example, approximately 2g fuel per 1g of NO_x were needed to achieve a 25 percent NO_x emission reduction over the AVL 8-mode heavy-duty test cycle. Assuming an engine of 6 g/bhp-hr NO_x and 300 g/bhp-hr BSFC, the associated fuel economy penalty would be 4 percent. More than twice as much fuel was needed to achieve a 40 percent NO_x reduction.

C 6.1.4. NO_x Adsorber Catalysts

NO_x adsorbers (lean NO_x traps) are the newest control technology being developed for partial lean burn, gasoline engines and for diesel engines. The adsorbers incorporated into the catalyst washcoat, chemically bind nitrogen oxides during lean engine operation. After the adsorber capacity is saturated or is at predetermined conversion efficiency, the system is regenerated, and released NO_x is catalytically reduced, during a period of rich engine operation or rich exhaust condition.

The NO_x adsorption/reduction mechanism is illustrated in Figure 2-56. The catalyst washcoat combines three active components: (1) an oxidation catalyst, for example Pt, (2) an adsorbant, for example barium oxide (BaO), and (3) a reduction catalyst, for example Rh.

The adsorption process involves two steps, which occur during lean engine operation. NO_x emissions from the diesel engine are typically composed of 90-95 percent nitric oxide, NO. In the first step, the nitric oxide reacts with excess oxygen on active oxidation catalyst sites (e.g. platinum, Pt) to form NO_2. The second step involves adsorption of the NO_2 by the storage material in the form of an inorganic nitrate.
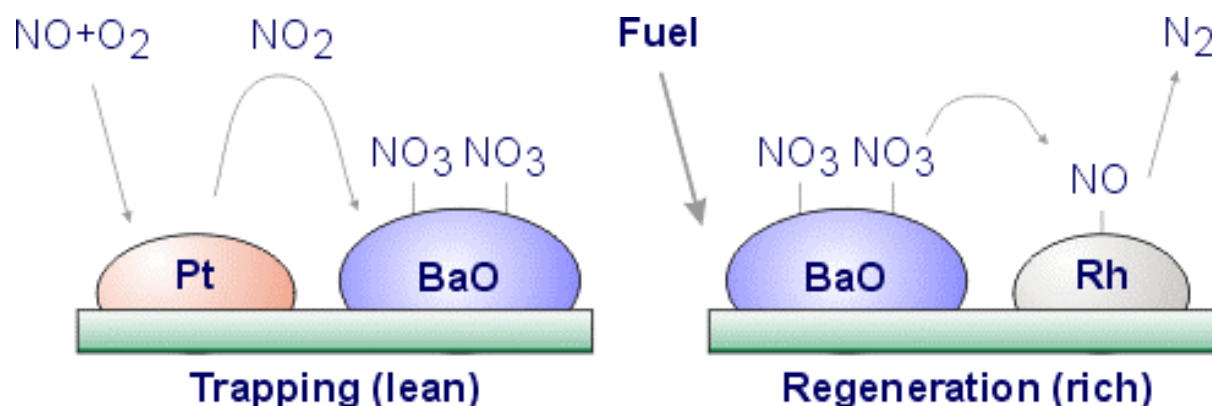
Figure 2-56. NO_x adsorption and reduction mechanism.

When the engine runs under excessive fuel conditions or at elevated temperatures the nitrate species become thermodynamically unstable and decompose, producing NO or NO_2.[93,94] Under rich conditions, nitrogen oxides are subsequently reduced by carbon monoxide, hydrogen, and hydrocarbons to N_2 over the reduction catalyst, in a conventional three-way catalyst process. This simplified set of reactions allows for an understanding of the basic NO_x adsorber chemistry. A more detailed analysis should also include other reaction paths and species, for example carbonates that may be formed in reactions between barium nitrate and carbon dioxide.[95]

NO_x adsorbers also show some undesired reactivity, primarily in regards to sulfur compounds which are present in exhaust gases from both diesel and gasoline engines. First, sulfur dioxide is oxidized to sulfur trioxide over platinum. Then, the SO_3 reacts with BaO to form barium sulfate. This causes gradual saturation of the barium sites with sulfur and loss of activity towards the adsorption of NO_2. $BaSO_4$ can be thermally decomposed. However, sulfates of barium and other NO_x adsorber compounds are more stable than their nitrates and require much higher temperatures to desulfate. For this reason, sulfur deactivation is the major problem in the development of NO_x adsorber systems.

There are a number of other possible reactions in NO_x adsorbers that can produce secondary, unregulated emissions. These are mainly reduction processes, also known to occur in the three-way catalyst, which involve NO/NO_2, as well as SO_2, and generate products other than nitrogen. The main secondary emissions include nitrous oxide (N_2O), ammonia (NH_3), and hydrogen sulfide (H_2S). NO_x adsorber catalysts exhibit high NO_x conversion efficiencies, in excess of 80-90 percent, as illustrated by example data in Figure 2-57. The activity of NO_x adsorbers covers a fairly wide catalyst *temperature window*, extending from about 200°C to 450-500°C. The lower end of the temperature window, T_1, is determined by the catalyst activity in regards to the oxidation of NO to NO_2, as well as NO_x release and reduction (3-way function). The upper temperature, T_2, is related to the thermodynamic stability of nitrates,

which undergo thermal decomposition at higher exhaust temperatures, even under lean conditions.
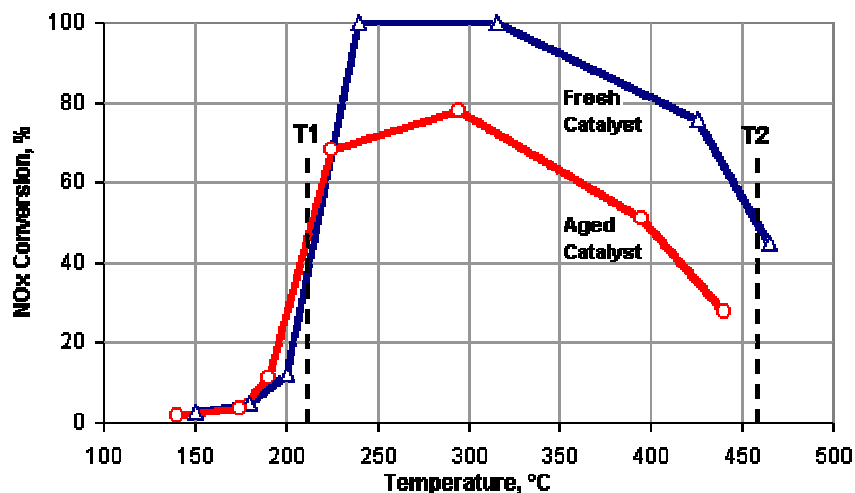
Figure 2-57. NO$_x$ adsorber conversion efficiency and operating range.

During the adsorption cycle, the adsorber is gradually converted into its nitrate form (e.g., barium nitrate) and the adsorption capacity becomes saturated. At this time the stored NO$_x$ needs to be released and catalytically reduced in a process called the regeneration. At lean exhaust conditions, barium nitrate decomposes at temperatures above 450 - 500°C. The regeneration occurs at much lower temperatures if a short pulse of fuel rich mixture is provided. NO$_x$ adsorbers can fully regenerate at 250°C, with the onset of a partial regeneration at temperatures as low as 150°C, if the air-to-fuel equivalence ratio is maintained at < 1.[96] Therefore, the operation of the adsorber catalyst system involves continuous cycling through lean and rich fuel condition.

The designer of an adsorber system has to analyze very carefully all pertinent operation temperatures, including exhaust gas temperatures during real life duty cycle and during the emission certification test, the NO$_x$ adsorber temperature window, the rich regeneration temperature, and the lean decomposition temperature. It is important, that adsorber temperatures during lean operation are below the thermal decomposition temperature of the stored nitrate (e.g., barium nitrate). Otherwise, NO$_x$ may be released at lean, leading to a decrease in the average conversion efficiency. While diesel adsorbers rarely see temperatures of 450 - 500°C, especially if installed away from the exhaust manifold, this may be a problem with gasoline engines, which experience higher combustion temperatures.

An example of lean/rich cycling is illustrated in Figure 2-58, which shows concentrations of NO$_x$ upstream and downstream of the adsorber, and the exhaust gas temperature.[97] The data was generated on a light-duty DI diesel engine. Rich spikes were achieved by simple throttling of the intake air, resulting in an oxygen concentration decrease to below 0.4 percent. The 60-second storage/regeneration pattern used during the test is visible in the peaks in NO$_x$ concentration. Engine out NO$_x$ shows minimums, which are caused by lower pressures/temperatures in the combustion chamber during intake air throttling. The tailpipe NO$_x$, on the other hand, shows maximums that represent the portion of released NO$_x$ which

has not been reduced over the rhodium catalyst. The engine was tested at a constant speed, but different, steady state torque levels resulting in stepwise changes in the exhaust temperature (red line in the graph).

At the highest tested temperature of about 330°C the adsorber catalyst achieved 95 percent NO_x conversion efficiency. As the exhaust temperatures were lowered, the conversion gradually decreased to reach about 50 percent at about 200°C. The declining catalyst efficiency manifests itself by increasingly higher tailpipe NO_x peaks during regeneration, as can be seen in Figure 2-58.
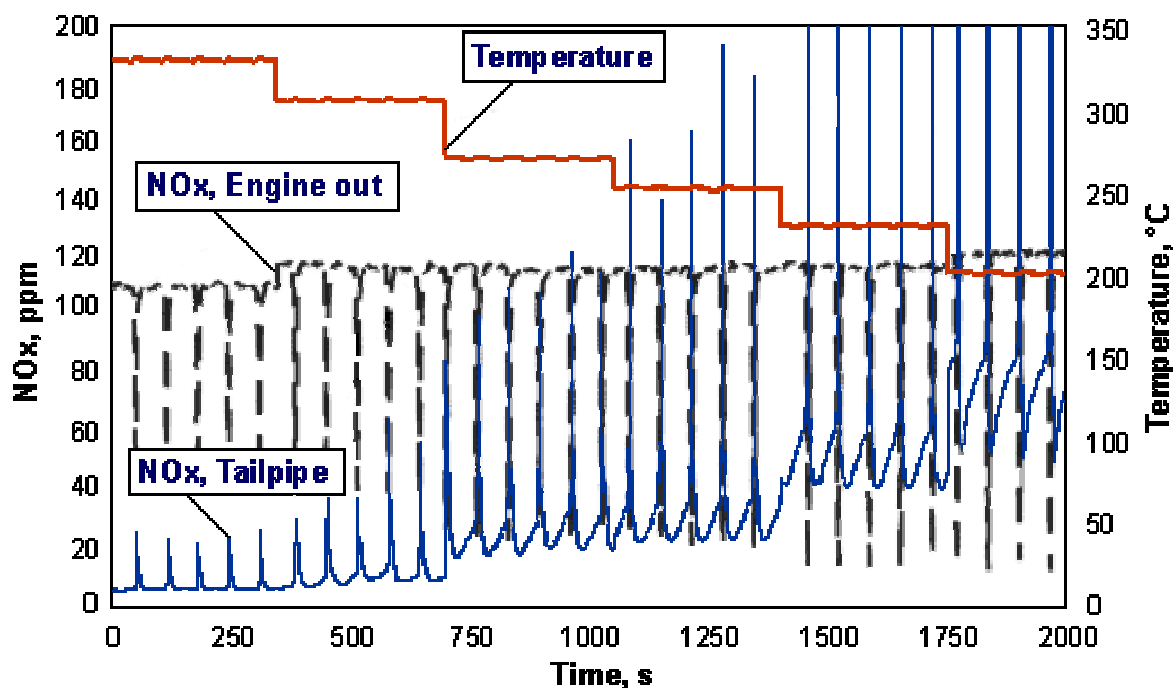
Figure 2-58. NO_x adsorber regeneration.

Diesel exhaust contains certain quantities of sulfur, primarily as sulfur dioxide, derived from diesel fuel and engine lubricating oil. In the presence of an oxidation catalyst, these compounds form stable sulfates with the NO_x storage materials. The adsorption of sulfur is preferential over the adsorption of NO_x. As a result, the catalyst performance gradually declines as fewer sites are available for NO_x adsorption.

Higher levels of sulfur in fuel result in faster and more severe deactivation, as shown in Figure 2-59.[98] It should be realized, however, that even sulfur levels less than 10 ppm eventually lead to NO_x adsorber poisoning, not to mention sulfur contribution from the engine lube oil.[99] Ultra low sulfur fuels are the necessary condition for implementation of this technology, but even if such fuels are available NO_x adsorbers are still likely to require some form of desulfation mechanism.

Sulfur poisoning begins on the surface of the catalyst inlet and progresses deeper into the washcoat and in the axial direction.[99,100] Sulfates derived from the known NO_x storage

materials are more thermally stable than the corresponding nitrates. They do not decompose at conditions that are usually encountered during adsorber operation, including both the adsorption and NO_x regeneration cycles. The problem of sulfur deactivation is equally affecting the diesel and GDI engine applications.
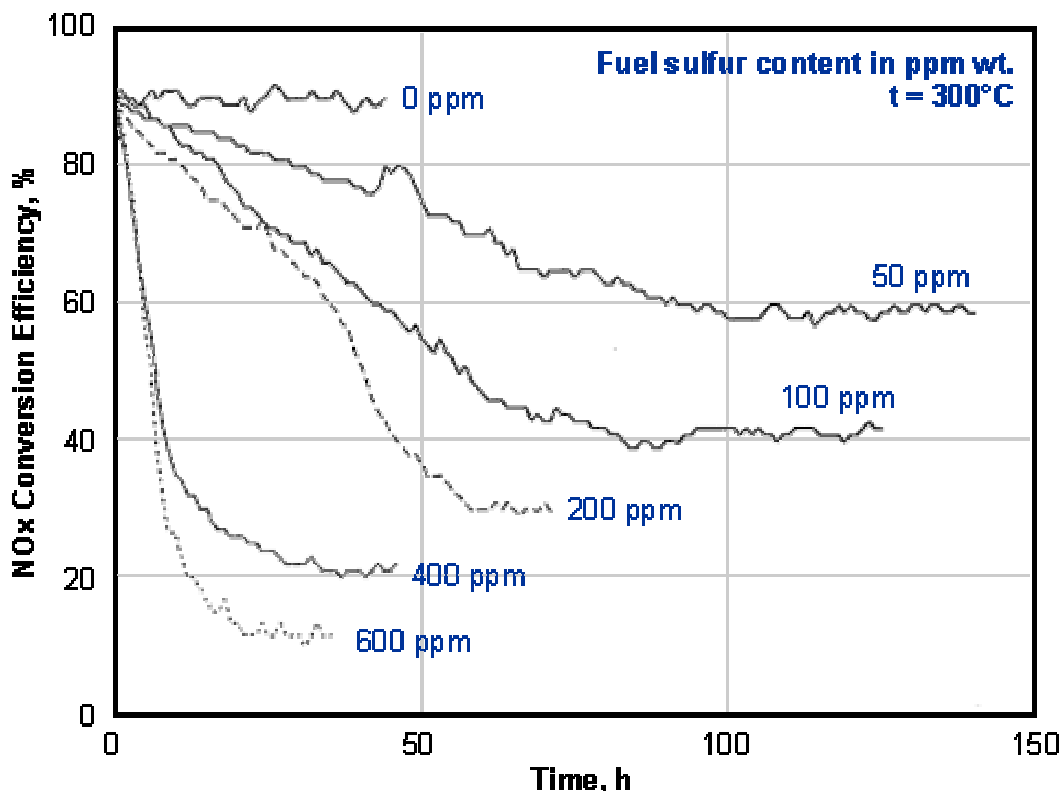
Figure 2-59. NOx adsorber efficiency at various fuel sulfur levels.

In general, sulfur poisoning is reversible and site activity can be restored by a desulfation process. This process involves decomposition of the sulfate species. The desulfation of NO_x adsorbers requires temperatures between 500 and 700°C, accompanied by mixture enrichment. It was reported that optimum desulfation of barium NO_x adsorbers is achieved at 650°C and λ = 0.98.[101] Studies on gasoline engines have found that adsorber desulfation was most effective in the presence of H_2 and CO, with H_2 being more effective. However, H_2 desulfation produced a mixture of H_2S and SO_2, while only SO_2 was detected among desulfation products when CO was used.[94]

In theory, the desulfation of NO_x adsorbers can restore their full adsorption capacity. In practice, a permanent and irreversible poisoning of some barium sites has been reported.[100] Another source of permanent performance loss after repeated desulfation is thermal degradation of washcoat and catalyst materials due to high temperatures during the desulfation process.[102] The desulfation strategy is a critical function in the NO_x adsorber design, still far from being solved, especially on diesel engines.[103] If sulfates are left in the catalyst for prolonged periods of time, the NO_x conversion efficiency is compromised. Frequent desulfation, on the other hand, may involve significant fuel economy penalties and accelerated thermal deterioration of the catalyst.

Various methods of desulfation through the increase of exhaust gas temperatures have been under development. For diesel engines, exhaust temperatures can be increased by post-injections of fuel. Algorithms have been developed which facilitated catalyst desulfation through system integration with the engine control unit, the common-rail fuel injection system, and the on-board diagnostics. Desulfation strategies for gasoline engines can also include a rapid, large amplitude modulation of the air-to-fuel ratio to create exothermal reactions increasing the catalyst temperature and minimizing H_2S release.[104] A desulfation strategy involving short A/F ratio pulses has been also proposed for the diesel engine. A desulfation through a series of short rich pulses, rather than a single, continuous rich period, allowed to minimize both H_2S emission and fuel economy penalty (reported at 1 percent when using 10 ppm S fuel). The pulses of $\lambda = 0.95$ and 30 s duration were repeated every 250 s over a nearly 1 hour long desulfation process.

A NO_x adsorber desulfation strategy was also developed and demonstrated on a diesel engine by the DECSE program (U.S. DOE).[105,106] The strategy, developed for a single point on the engine map of exhaust temperature of 400°C, involved a common rail post-injection and a close-coupled warm-up catalyst. Hydrocarbons generated through the post-injection were oxidized in the warm-up catalyst to create an exotherm increasing the NO_x adsorber inlet temperature to 700°C (Figure 2-60).
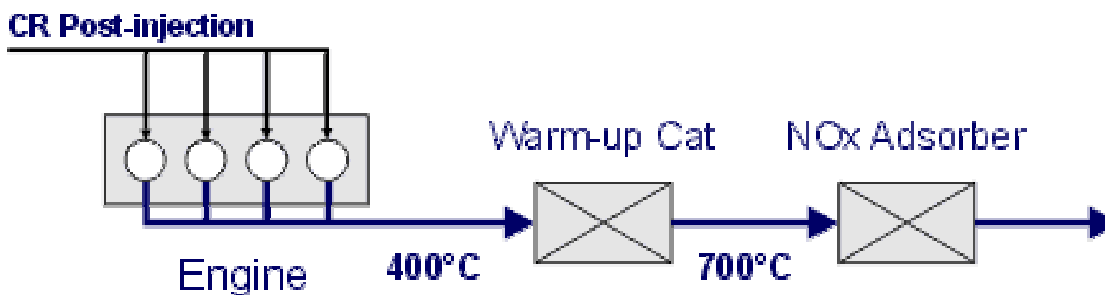
Figure 2-60. Schematic of the DECSE desulfation process.

DECSE experiments to develop the strategy were conducted by operating the engine on commercial, 380 ppm S fuel for approximately two hours, until the initial NO_x conversion efficiency of 80 percent dropped to 60 percent due to sulfur poisoning. At that moment, the desulfation event was triggered. The adsorber inlet temperature of 700°C was achieved 90 - 180 seconds after initiating the desulfation, depending on the post-injection quantity and the EGR rate (the quantity of 30 mm^3/stroke and the EGR of 26.6 percent were eventually selected). Restoring the NO_x efficiency to the original 80 percent required a duration of the desulfation event of about 5-6 minutes. The above procedure was applied a number of catalysts of different poisoning histories, all of which were restored to over 85 percent NO_x reduction efficiency over the catalyst inlet operating temperature window of 300°C - 450°C. This performance level was achieved while staying within the 4 percent fuel economy penalty target defined for the adsorber regeneration. Variations of the engine torque due to post-injections during the desulfation event were controlled within 1 percent.

Mixture enrichment ($\lambda < 1$) on lean burn gasoline engines may require, in order to minimize torque disturbances, some coordination of spark advance with fuel injection, but otherwise

seems to be fairly straightforward. Generation of rich air-to-fuel mixtures on the diesel engine, which normally operates at $\lambda => 1.3$ and leaner, is certainly more challenging.

Theoretically, the methods of diesel mixture enrichment can be grouped into two categories, as follows:

> 1) Exhaust gas enrichment
>
> 2) In-cylinder enrichment

Exhaust system enrichment may be realized through injection of diesel fuel upstream of the catalyst, in a similar manner as it was suggested in active lean NO_x catalysts, which work through selective NO_x reduction by hydrocarbons. However, efficient NO_x adsorber regeneration requires not only the presence of reductants, but also the absence of oxygen. In the case of exhaust enrichment, the existing oxygen needs to be combusted to CO_2 and H_2O before NO_x conversion can proceed. This can be realized in the NO_x adsorber itself, or in an upstream oxidation catalyst. Disadvantages of this process include exotherms, which can be damaging to the catalyst, and an additional fuel economy penalty.

Theoretically, reducing gases other than hydrocarbons derived from the diesel fuel can be also used for the regeneration of NO_x adsorbers. Regeneration of a NO_x adsorber through the injection of syngas ($CO+H_2$) into the exhaust system was demonstrated on a light duty vehicle.[107] In practical applications, the reductants would have to be generated on-board by reforming diesel fuel. It was proposed that hydrogen-rich gas ($CO+H_2$) be produced from diesel fuel by electric discharge (plasma) continuously applied to flowing fuel/air mixture in a device termed the "diesel plasmatron reformer."[108]

In-cylinder enrichment involves such methods as altering fuel injection timing and rate, throttling, and using EGR.[109] Advanced, electronically controlled diesel fuel injection systems, such as the common rail, can now offer much more flexibility for practical in-cylinder enrichment strategies. The common rail is the first diesel injection system in which both the injection rate and timing can be controlled totally independent of the engine speed and load condition. In particular, it is possible to provide post-injections of fuel, as may be required to increase the exhaust gas temperature.

Common rail injection has already been used for increasing diesel exhaust gas temperature as a means of assisting the regeneration of a particulate filter.[110] The task was accomplished with three injections and required a turbocharger adjustment in order to maintain torque. The filter application, however, differs from that of the NO_x adsorber in the fact that quantities of oxygen remain in the exhaust gas. Systems specifically developed for regeneration of NO_x adsorbers are likely to require a combination of methods, e.g., implementing intake air throttling in addition to multiple injections.[111]

A new diesel combustion process, called the "low temperature combustion", has been developed by Toyota for the regeneration of NO_x adsorbers at low load and speed conditions in light-duty engines. The process involves massive EGR, intake air throttling, and injection timing designed for smokeless combustion despite rich A/F ratio. This new combustion process is sometimes referred to generically as homogeneous charge compression ignition

(HCCI) and some variations of that system are referred to as partial premixed compression ignition (PPCI).

One of the most important aspects of utilizing NO_x adsorber technology is to establish engine operating conditions that would facilitate a satisfactory level of NO_x conversion through proper adsorber regeneration and desulfation, while minimizing the associated fuel economy penalty. This optimization is achieved by defining a lean/rich modulation strategy, while paying close attention to resulting NO_x, CO, and HC concentrations, as well as to exhaust temperatures. More fuel-rich modulations typically result in faster and more complete regeneration of the adsorber and, thus, in higher average NO_x conversion efficiencies.

The DECSE program concluded, that an over 80 percent peak NO_x conversion efficiency can be achieved at a fuel economy penalty of less than 4 percent.[112] While the 4 percent figure provides a useful reference number on the anticipated fuel cost of this technology, there is still room for optimization of the engine-catalyst system. This is best illustrated in Figure 2-61, taken from the same DECSE study. Two NO_x conversion curves shown in the graph were generated using two different engine calibrations. In both cases the fuel penalty was kept below 4 percent and identical rich/lean timing was used, but different NO_x conversions were seen. It is clear that the regeneration cycle modulation has to be very carefully tuned to match the catalyst requirement; otherwise, quantities of fuel may be wasted through unproductive mixture enrichment.
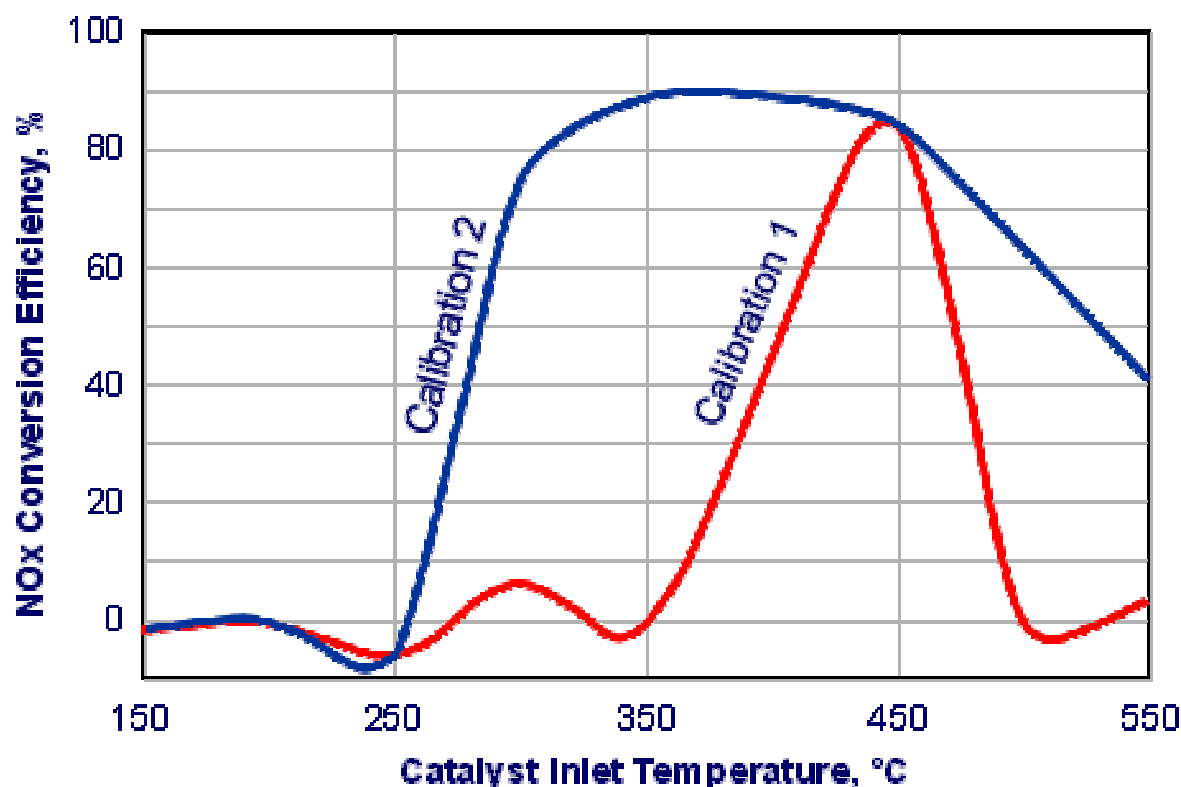
Figure 2-61. Influence of calibration on NOx conversion efficiency.

While most of the early laboratory studies were performed at steady-state conditions, real-life NO$_x$ adsorber systems must provide efficient NO$_x$ reductions at all operating conditions, including engine transients. The regeneration and desulfation cycles in high efficiency systems require a *closed-loop control*, based on the concentrations of NO$_x$ and oxygen, temperature, and other parameters. The feedback signals must be provided by sensors, including *NO$_x$ sensors* and *A/F ratio sensors*. The control system, integrated with the engine control module, has to determine the regeneration and desulfation parameters (timing, duration, A/F ratio, …) and the enrichment strategy depending on the process variables and the engine operating conditions. The optimization of the regeneration/desulfation control and the integration of the engine-catalyst system remain perhaps the most challenging task on the road towards commercial introduction of NO$_x$ adsorbers.

Since the late 1990's, a notable progress has been achieved in the integration of NO$_x$ adsorbers with diesel fueled vehicles, especially in light-duty applications for the European and Japanese markets. As the research progresses, there are more attempts to demonstrate NO$_x$ adsorber systems on diesel engines, including heavy-duty applications targeting the US2007/2010 standards. Since NO$_x$ adsorbers can only be effective in controlling NO$_x$, CO, HC, and SOF emissions, particulate filters will be required for PM reductions needed to meet emission standards (Euro5, US2007/2010, Tier2). For this reason, any serious demonstration programs need to integrate NO$_x$ adsorbers with diesel particulate filters (DPF). There are at least two such integrated emission control systems, one for heavy- and one for light-duty engines that deserve more detailed discussion:

- EPA 2007/2010 "Proof-of-Concept" system has been developed as a laboratory demonstration of the technical feasibility of the US2007 emission standards. While not optimized and far from mature, the system became a benchmark and a starting point for NO$_x$ adsorber-based emission control system development by U.S. heavy-duty engine manufacturers.

- Toyota DPNR system is perhaps the most advanced NO$_x$ adsorber system, which is nearing a commercial deployment on diesel cars. VThe DPNR features a very elegant and compact integration of a diesel particulate filter and the NO$_x$ adsorber, with the latter being simply coated on the filter substrate.

EPA 2007 Proof-of-Concept: One of the first NO$_x$ adsorber demonstrations on a heavy-duty engine was presented by the U.S. EPA as a "proof-of-concept" for the US2007/2010 HD diesel emission standards (NO$_x$ = 0.2 g/bhp-hr; PM = 0.01 g/bhp-hr).[113] The system, installed on a production Cummins ISB engine (5.88 liter, 6-cylinder, turbocharged-aftercooled, DI, 4 valves per cylinder, 194 kW/260 hp @2500 rpm), included two catalyzed DPF - NO$_x$ adsorber banks in parallel, as shown in Figure 2-62 and in Figure 2-63. The exhaust flow was periodically switched through a valving system to direct most of the flow to the adsorber in operation, and only a small portion of the gas stream to the adsorber in regeneration. A secondary fuel injection was applied during regeneration upstream of the DPF. The injected fuel was oxidized over the DPF catalyst, depleting oxygen and increasing the temperature. An oxidation catalyst, shared by both DPF/adsorber banks, was included at the end of the system to control HC emissions that may have broken through the regenerating adsorber. The system also included a number of zirconia NO$_x$ sensors (before DOC, after

adsorbers, in the engine exhaust manifold) and oxygen sensors (after adsorbers) to provide feedback for the control system.

The EPA system provided impressively high conversion levels of 98 percent reduction in NO_x (down to 0.25 g/bhp-hr) and 93 percent reduction in PM (0.002 g/bhp-hr), as measured over the FTP transient cycle. The engine was operated on a 5 ppm sulfur fuel. A fuel economy penalty of 2.3 percent was attributed to the regeneration of the NO_x adsorber (this figure did not include any penalties that may have resulted from the system pressure drop). An oversized catalyst system, including 70 liters of combined catalyst/DPF volume, was used in the study. No adsorber desulfation tests were conducted; adsorber deactivation by sulfur would eventually occur in real life, even when using diesel fuel of only 5 ppm sulfur.
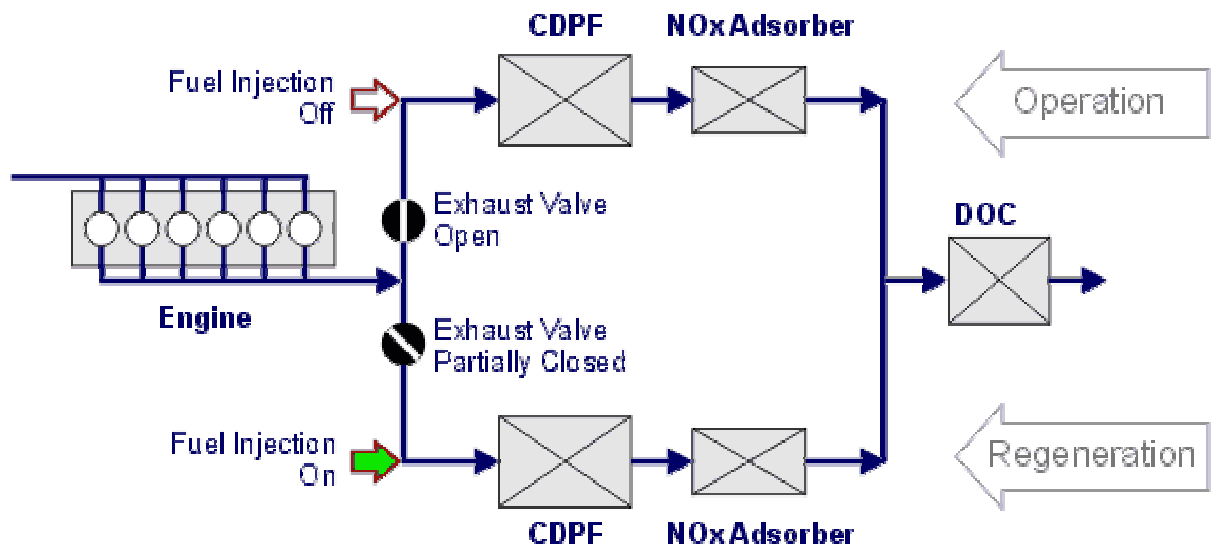
Figure 2-62. NOx adsorber system in EPA's 2007/2010 "proof-of-concept" study.

Figure 2-63. Photograph of the NO$_x$ adsorber system in EPA's study.

In the second stage of the study, the engine was modified by adding a high pressure common-rail injection system with a Bosch/ETAS engine management system, and a high pressure loop EGR.[114] In this configuration, the adsorber system yielded an average NO$_x$ emission of 0.13 g/bhp-hr (down from a 2.67 g/bhp-hr baseline) over a hot start FTP test at a reductant fuel economy penalty of 1.49 percent.

The dual adsorber/DPF bank approach allows minimizing the fuel economy penalty by regenerating the adsorber at a low exhaust gas flow, however, it results in a very large total catalyst volume. Reduction in the system size may be realized by decreasing the catalyst volume, as well as by optimizing the split between the catalyst volume in the operation and regeneration modes. The system shown in Figure 2-63 includes equal volumes in each mode. However, the regeneration time that is required for the NO$_x$ adsorber is shorter than the time needed to saturate the adsorber with NO$_x$. This results in a part of the system volume "idling" after the regeneration cycle is completed. The EPA system size would be further reduced if the regeneration was conducted using a smaller proportion of the total catalyst volume. The EPA planned on splitting the system into four sections, three of which would be in the operation mode, while one would be regenerated. Exhaust gas flow would be directed to the proper section(s) using a rotary valve system upstream of the filter/catalyst body. The standard truck muffler visible on the floor underneath the system in Figure 2-63 represents the target volume for the entire system utilizing that concept.

The EPA system configuration, based on a production diesel engine, it is an example of a retrofit NO$_x$ adsorber system. In future engines, the adsorber management strategy will be

integrated with that of the engine, thus allowing for the optimization of the regeneration process and, preferably, allowing for use of single bank configuration of much smaller catalyst volume.

Toyota DPNR System: A very elegant and compact system, combining a NO_x adsorber and a DPF on one substrate was developed by Toyota and termed Diesel Particulate-NO_x Reduction system, or DPNR.[115,116,117] The DPNR utilizes a cordierite wall-flow particulate filter, with channels are alternatively plugged at the ends to force the gas through the porous walls, where the particulates are mechanically trapped. The NO_x adsorber catalyst is coated on the filter substrate, over the channel walls and inside the pores. The system adsorbs and reduces NO_x over a lean-rich modulation cycle typical for NO_x adsorbers. Particulate matter collected on the filter is continuously regenerated over the Pt-containing catalyst, just as is the case in catalyzed particulate filters. Interestingly, a synergistic effect was found between the NO_x and PM control functions in the DPNR, with the rich pulsing enhancing the filter regeneration process.

A schematic of the DPNR system integrated with a prototype diesel engine is shown in Figure 2-64. The engine (in-line 4 cylinder, 2.0 liter, water-cooled, TDI) is equipped with a common-rail fuel system and cooled, high-pressure loop EGR. The NO_x adsorber/DPF unit is installed downstream of the turbocharger. The reported volume of the DPNR substrate varies between 1 - 1.5 times the engine displacement; it was 2.8 liter in the system in Figure 2-64. A substrate geometry of 300 cpsi, 0.3 mm wall thickness, 55% porosity, and a relatively large mean pore size of 25 μm to enable catalyst coating was reported. The DPNR substrate is followed by an oxidation catalyst, which removes HC emissions that may pass through the NO_x adsorber during regeneration. The engine is also equipped with a fuel injector in the exhaust manifold. A number of sensors are needed to provide feedback to the engine controller, including gas temperature, DPNR pressure drop, intake air flow, and A/F ratio sensors, as shown in the schematic.
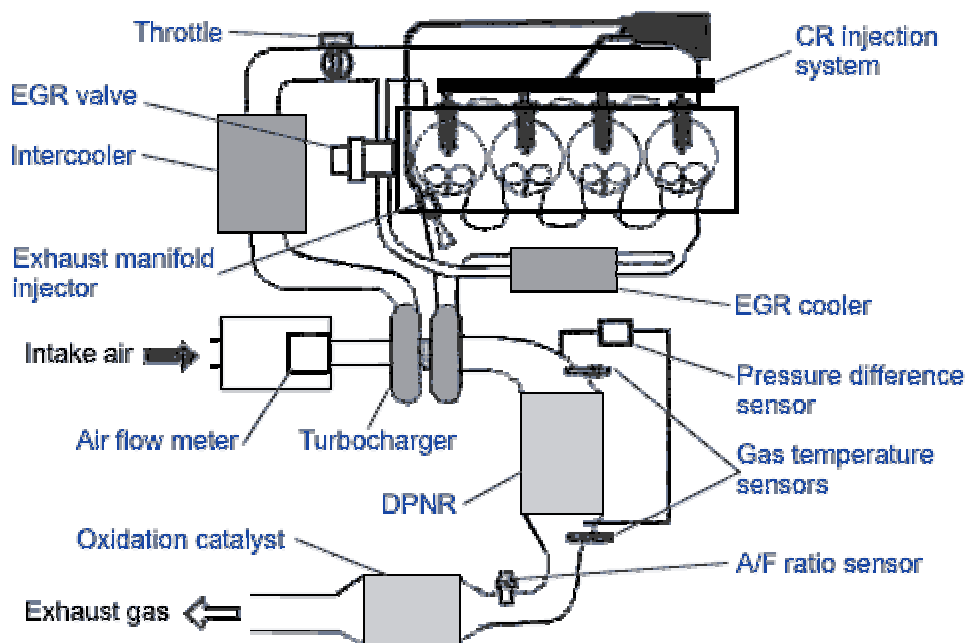
Figure 2-64. Schematic of the Toyota DPNR system.

Parameters of the NO_x adsorber operation varied in particular tests, but have been generally reported around 60 s lean operation, followed by 1 - 3 s rich pulse at A/F = 11.5 - 12.5.[117] Most testing has been performed with fuel of 30 ppm sulfur. Adsorber desulfation is performed at around stoichiometric condition over a period of about 50 seconds and catalyst bed temperature of about 600°C. H_2S emissions during desulfation are minimized by lean-rich switching. The PM regeneration in the filter is controlled through the A/F ratio which impacts the catalyst temperature through both the exhaust gas temperature and the temperature increase in the catalyst due to HC oxidation. The control of the A/F ratio involves three mechanisms, as follows:

1) "Low temperature combustion" (high EGR + injection timing + intake air throttle)

2) Post-injection of fuel to the engine cylinders

3) Exhaust manifold injection of fuel

The combination of control mechanisms depends on the engine operating condition, as well as on the state of the DPNR system. For instance, increased temperatures are needed to force the PM oxidation if the filter becomes overloaded with soot. The DPNR control strategies are illustrated in Figure 2-65.[118] It was found that the rich pulsing enhances the oxidation of PM, thus making it possible to reliably control the filter regeneration at widely ranging operating conditions. A switch-flow version, in which the direction of flow through the filter could be reversed by a valve, was considered during early development but was later abandoned. The PM regeneration enhancement relative to conventional catalyzed filters is not entirely understood, but it may be attributed to a combination of several mechanisms, as follows:

1) Nitrogen dioxide, which is an intermediate product in the process of lean NO_x adsorption, is well known to enhance DPF regeneration.[119]

2) Toyota researchers found that active oxygen species which are formed during both NO_x adsorption and rich regeneration are very effective in soot oxidation.[117]

3) The PM oxidation rates were found to be higher with "fresh" soot, as it is the case with the continuously regenerating DPNR. Soot that may accumulate to higher loadings in conventional filters exhibits particle growth and collapsing of its micropore structure, both effects leading to slower oxidation rates. Maintaining low soot loadings also improves the contact between carbon particles and the catalyst.[117]

According to Toyota, a fresh DPNR catalyst can reduce both NO_x and PM emissions by over 80 percent. An aged catalyst achieved 0.13 g/km NO_x and 0.005 g/km PM over the ECE+EUDC cycle on a 1400 kg car.[118] Introduction of the DPNR system on production vehicles is expected in the near future.
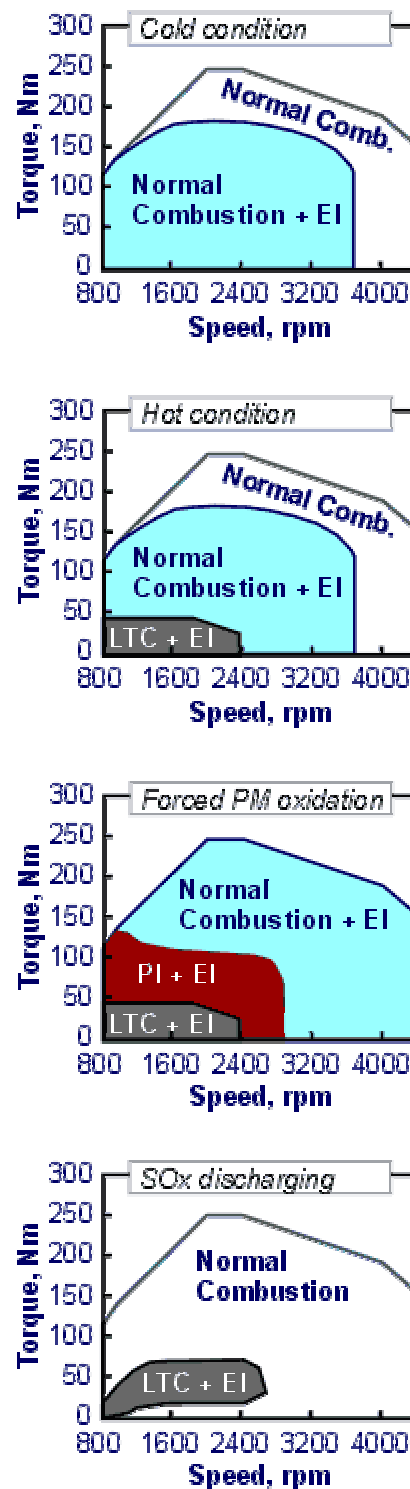
Figure 2-65. DPNR system control strategies.
(EI - exhaust manifold injection; PI - common rail post injection; LTC - low temperature combustion).

C 6.1.5. Issues With NO$_x$ Adsorber Catalysts

Before adsorber-catalysts can become a wide-spread commercial NO$_x$ control technology, more progress has to be made in the NO$_x$/SO$_x$ adsorber technology itself and, very importantly, in many areas relevant to the system integration with the diesel engine. The following is a summary of issues which need to be addressed:

1) Dual exhaust system configuration such as that demonstrated by EPA is not acceptable for the majority of heavy-duty applications.

2) Single exhaust system configuration such as demonstrated by Toyota may not be acceptable for all applications since it relies on LTC. This type of combustion is unproven for its potential impact on durability. Injection during or before the intake stroke may lead to lube oil contamination with fuel sprayed on the walls of the cylinder liners.

3) Fuel economy penalty associated with size-optimized systems may not be acceptable to heavy-duty customers. Conversely, larger catalyst and filter sizes required to minimize fuel economy degradation will not be acceptable as in Item 1 above.

4) Control requirements for the system operation necessitate using new and unproven sensor technologies such as NO$_x$ sensors.

5) Accuracy required to maintain conformance to EPA's 2007/2010 standards may not be available in the state-of-the-art sensor technology.

6) Costs associated with the new control requirements may be prohibitively high.

7) Methods of mixture enrichment need to be developed. Potential problems include torque/drivability issues and high PM and HC emissions during the enrichment.

8) NO$_x$ adsorber regeneration and desulfation strategies have to be developed. They will require a closed loop control in tight integration with the engine management and other vehicle systems, such as the on-board diagnostics.

9) Optimized NO$_x$ adsorbers in terms of adsorption capacity, rich regeneration temperatures, lean thermal stability, etc., are necessary for efficient application of the technology.

10) Secondary unregulated emissions, including H$_2$S and N$_2$O, from adsorber systems need to be minimized. Depending on the regeneration/desulfation strategies, adsorber systems may also produce off-cycle emissions of regulated pollutants.

11) Thermal durability of catalysts and resistance to poisons has to be demonstrated. The impact of phosphorus and zinc, known poisons of the 3-way catalyst, on NO_x adsorbers is still unknown.

Furthermore, the commercialization of this technology is only possible in conjunction with legislation and widespread availability of ultra low sulfur diesel fuels as well as sulfur-free lube oils.

C 6.1.5. Selective Catalytic Reduction

Selective catalytic reduction (SCR) of NO_x by nitrogen compounds, such as *ammonia* or *urea*—commonly referred to as simply "SCR"—has been developed for and well proven in industrial stationary applications. It has been used since the 1970's in such applications as plant and refinery heaters and boilers in the chemical processing industry, gas turbines, and coal-fired cogeneration plants. The list of fuels used in these applications includes industrial gases, natural gas, crude oil, light or heavy oil, and pulverized coal.[120]

The application of SCR for mobile diesel engines requires overcoming several problems, which are discussed later. Due to their active character, SCR emission control systems are likely to be complex and expensive. However, SCR is still the only catalyst technology capable of reducing diesel NO_x emissions to levels required by a number of future emission standards. Notably, SCR has been strengthening its position as the technology of choice for meeting the Euro V (2008) NO_x limit of 2 g/kWh for heavy-duty truck and bus engines. SCR systems for both heavy- and light-duty engines are currently being developed in Europe, as well as in the U.S. in the context of the 2007 NO_x limit of 0.2 g/bhp-hr. However, the U.S. clean air authorities have voiced concerns as to the enforceability of this technology. From the regulatory perspective SCR poses enforcement problems, both in terms of ensuring that the reductant is available together with diesel fuel throughout the nationwide distribution network, and that it is always timely replenished by vehicle operators.

Reductants and Catalytic Reactions: Two forms of ammonia may be used in SCR systems: (1) pure anhydrous ammonia, and (2) aqueous ammonia. Anhydrous ammonia is toxic, hazardous, and requires thick-shell, pressurized storage tanks and piping due to its high vapor pressure. Aqueous ammonia, $NH_3 \cdot H_2O$, is less hazardous and easier to handle. A typical industrial grade ammonia, containing about 27 percent ammonia and 73 percent water by weight, has nearly atmospheric vapor pressure at normal temperatures and can be safely transported on highways in the U.S. and other countries.

Several chemical reactions which occur in the ammonia SCR system are expressed by Equations (1) to (5). All of these processes represent desirable reactions that reduce NO_x to elemental nitrogen. Equation (2) is the dominant reaction mechanism.[121] Reactions given by Equation (3) through (5) involve nitrogen dioxide reactant. NO_2 concentrations in most flue gases, including diesel exhaust under normal conditions, are low. The importance of these reaction paths increases with feed gases containing increased levels of NO_2.

$$6NO + 4NH_3 = 5N_2 + 6H_2O \qquad\qquad (1)$$

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \qquad\qquad (2)$$

$$6NO_2 + 8NH_3 = 7N_2 + 12H_2O \qquad\qquad (3)$$

$$2NO_2 + 4NH_3 + O_2 = 3N_2 + 6H_2O \qquad\qquad (4)$$

$$NO + NO_2 + 2NH_3 = 2N_2 + 3H_2O \qquad\qquad (5)$$
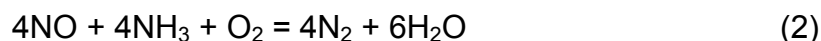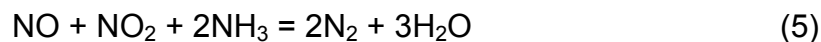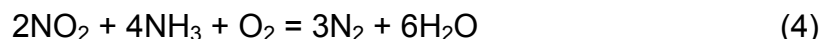
Undesirable processes occurring in SCR systems include several competitive, nonselective reactions with oxygen, which is abundant in the system. These reactions can either produce secondary emissions or, at best, unproductively consume ammonia. Partial oxidation of ammonia, given by Equations (6) and (7), may produce nitrous oxide (N_2O) or elemental nitrogen, respectively. Complete oxidation of ammonia, expressed by Equation (8), generates nitric oxide (NO).

$$2NH_3 + 2O_2 = N_2O + 3H_2O \qquad\qquad (6)$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \qquad\qquad (7)$$

$$4NH_3 + 5O_2 = 4NO + 6H_2O \qquad\qquad (8)$$
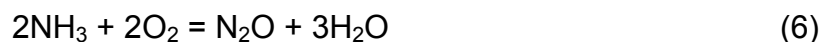
At low temperatures, below about 100-200°C, ammonia can also react with NO_2 producing explosive ammonium nitrate (NH_4NO_3):

$$2NH_3 + 2NO_2 + H_2O = NH_4NO_3 + NH_4NO_2 \qquad\qquad (9)$$
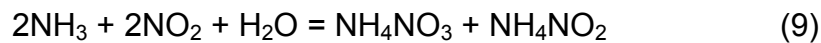
This reaction can be avoided by making sure that the temperature never falls below about 200°C. The tendency of NH_4NO_3 formation can also be minimized by supplying into the gas stream less than the precise amount of NH_3 necessary for the stoichiometric reaction with NO_x (1 to 1 mole ratio).

When the flue gas contains sulfur, as is the case with diesel exhaust, SO_2 can be oxidized to SO_3 with the following formation of H_2SO_4 upon reaction with H_2O. These reactions are the same as those occurring in the diesel oxidation catalyst. In another reaction, NH_3 combines with SO_3 to form $(NH_4)_2SO_4$ and NH_4HSO_4, Equation (10) and (11), which deposit on and foul the catalyst, as well as downstream piping and equipment. At low exhaust temperatures, generally below 250°C, the fouling by ammonium sulfate may lead to a deactivation of the SCR catalyst.[122]

$$NH_3 + SO_3 + H_2O = NH_4HSO_4 \qquad\qquad (10)$$

$$2NH_3 + SO_3 + H_2O = (NH_4)_2SO_4 \qquad\qquad (11)$$
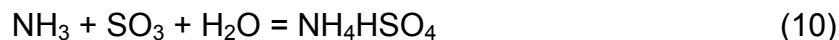
The SCR process requires precise control of the ammonia injection rate. An insufficient injection may result in unacceptably low NOx conversions. An injection rate which is too high results in release of undesirable ammonia to the atmosphere. These ammonia emissions from SCR systems are known as *ammonia slip*. The ammonia slip increases at higher NH3/NOx ratios. According to the dominant SCR reaction, Equation (2), the stoichiometric NH3/NOx ratio in the SCR system is about 1. Ratios higher than 1 significantly increase ammonia slip. In practice, ratios between 0.9 and 1 are used, which minimize the ammonia slip while still providing satisfactory NOx conversions. Figure 2-66 presents an example relationship between the NH3/NOx ratio, NOx conversion, temperature, and ammonia slip.[123] It should be noted that ammonia slip decreases with increasing temperature, while the NOx conversion in an SCR catalyst may either increase or decrease with temperature, depending on the particular temperature range and catalyst system, as will be discussed later.
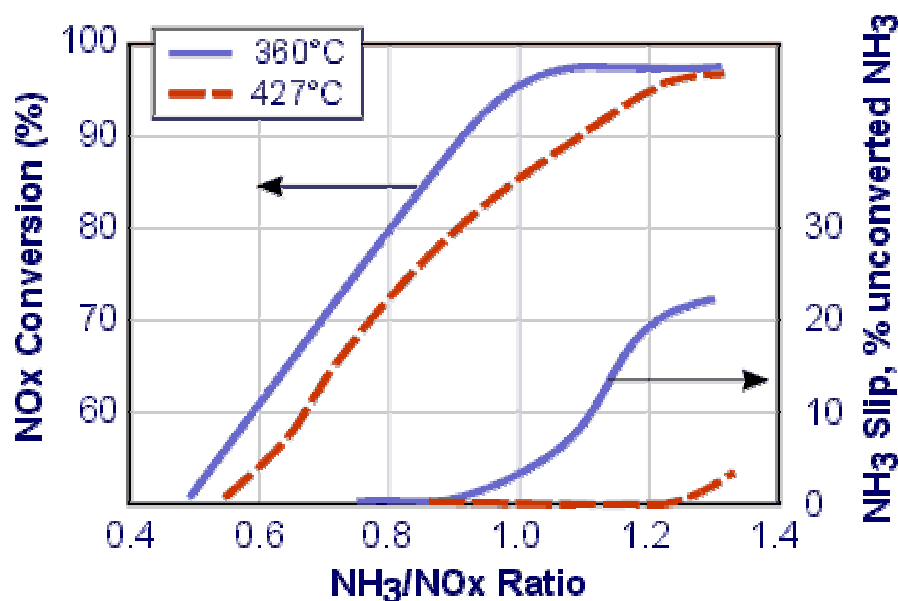
Figure 2-66. NOx Conversion and ammonia slip for different NH3/NOx ratios. *(V2O5/TiO2 SCR catalyst, 200 cpsi).*

In stationary applications, the maximum permitted NH3 slip is always specified, with a typical specification at 5-10 vppm NH3. These concentrations of ammonia are generally undetectable by the human nose. Optionally, ammonia slip can be also controlled by a cleanup catalyst (oxidation catalyst) installed downstream of the SCR catalyst.

Urea: Due to the toxicity and handling problems with ammonia, there is a need for more convenient SCR reductants. From the technical point of view, the alternative reductant has to easily and completely decompose to ammonia, producing no harmful by-products, under the conditions in the SCR reactor. From the commercial perspective, the perfect reductant would be non-toxic, easy to transport and handle, inexpensive and commonly available. The most widely accepted reductant is urea, $CO(NH_2)_2$. Other alternatives that have been considered include carbamate salts, e.g. ammonium carbamate, NH_2COONH_4.[124]

Urea meets the criteria of non-toxicity and safety in handling and transportation and is commercially available. For these reasons, urea is now practically the only reductant considered for use in mobile SCR applications. Water solutions appear to be the preferred form of urea. The use of solid urea has been suggested but so far the idea seems to be gaining little acceptance.

Urea is a commodity, produced in large scale. Worldwide demand is estimated at 100 million ton/year, compared to a production capacity of 133 million ton/year.[126] It is used primarily in the food processing and fertilizer industries. Under normal conditions urea is a solid substance. Even though the solubility of urea in water is better than 50 percent (108 g/100 ml H_2O at 20°C), aqueous urea solutions used in SCR systems have typically a concentration of 32.5 percent by weight. At this concentration urea forms an eutectic solution characterized by the lowest crystallization point of -11°C. The use of eutectic solution provides an additional advantage of equal concentrations in the liquid and solid phases during crystallization. Even if partial freezing occurred in the urea tank, crystallization would not change the concentration of urea solution fed to the SCR system.

Currently, there is no industry standard for urea used in SCR applications. Specification of aqueous urea which was used by Siemens in SCR demonstration programs with highway diesel engines is shown in Table 2-13.[127,128]

In the SCR process, water solutions of urea are injected into the process gas stream. At temperatures above 160°C urea starts to decompose and hydrolyze according to the following reaction equations:

$$CO(NH_2)_2 = 2 \cdot NH_2 + CO \qquad\qquad (12)$$

$$CO(NH_2)_2 + H_2O = 2NH_3 + CO_2 \qquad\qquad (13)$$
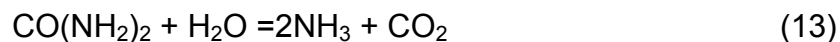
The thermal decomposition, Equation (12), is confirmed by an evidenced formation of CO during SCR processes with urea.[129,130] The $\cdot NH_2$ radical can then react with NO as follows:

$$NH_2 + NO = N_2 + H_2O \qquad\qquad (14)$$

If urea is fed into the system at lower temperatures, it may foul and deactivate the catalyst, presumably due to the production of polymeric species which mask the catalyst surface. This may be a serious consideration for low temperature applications.

Table 2-13. Specification of aqueous urea for SCR applications.

Property	Value
Name	Aqueous urea solution
CAS #	57-13-6
Chemical formula	$(NH_2)_2CO \cdot H_2O$
Molecular weight (anh. urea)	60.06 kg/kmole
Urea content	32.5 +/-0.5%
Density at 15°C	1085 kg/m^3
PH	9 - 11
Appearance	Colorless
Point of crystallization	-11°C
Alkalinity as NH_3	Max. 0.4%
Carbon as CO_2	Max. 0.4%
Biuret	Max. 0.4%
Calcium	Max. 1 mg/dm^3

Some SCR systems proposed for mobile applications include a dedicated urea hydrolysis catalyst placed between the urea injection point and the SCR catalyst.[131] Hydrolysis catalysts selectively promote urea hydrolysis according to Equation (13).

Ammonia generated from the hydrolysis of urea reacts with NO_x according to the already discussed reactions, Equation (1) - (5). It can be calculated from Equation (13) that 1 kg of urea is equivalent to 0.566 kg of ammonia reagent. This ratio represents the stoichiometric requirement for pure urea reactant. For 32.5 percent urea solution, 1 kg of the solution is equivalent to 0.184 kg of ammonia.

Types of SCR Catalysts: The selective catalytic reduction of NO_x with ammonia was first discovered over a platinum catalyst. The Pt technology can be used only at low temperatures (< 250°C), due to its poor selectivity for NO_x reduction at higher temperatures. Base metal catalysts have higher SCR temperature windows. A comparison of the operating temperature ranges for various catalyst technologies available for SCR NO_x is shown in Figure 2-67.[132]

Platinum catalysts lose their NO_x reduction activity above approximately 250°C. A V_2O_5/Al_2O_3 catalyst was used first for higher temperature applications. However, its use was limited to sulfur free exhaust gases because the alumina reacted with SO_3 to form $Al_2(SO_4)_3$, resulting in catalyst deactivation. To solve this problem, a non-sulfating TiO_2 carrier was used for the V_2O_5, which then became the catalyst of choice. These catalysts functioned at higher temperature and over a broader temperature range than Pt. Other base metal oxides, such as tungsten trioxide (WO_3) and molybdenum trioxide (MoO_3), are often added to V_2O_5 as promoters to further decrease the SO_3 formation and to extend catalyst life. Finally, zeolite based catalysts have been developed that function at high temperatures. The active catalytic components and the corresponding temperature ranges are classified in Table 2-14. These temperature ranges should be considered approximate. Catalysts are under development, especially for mobile SCR applications, which are characterized by increasingly wider temperature windows.
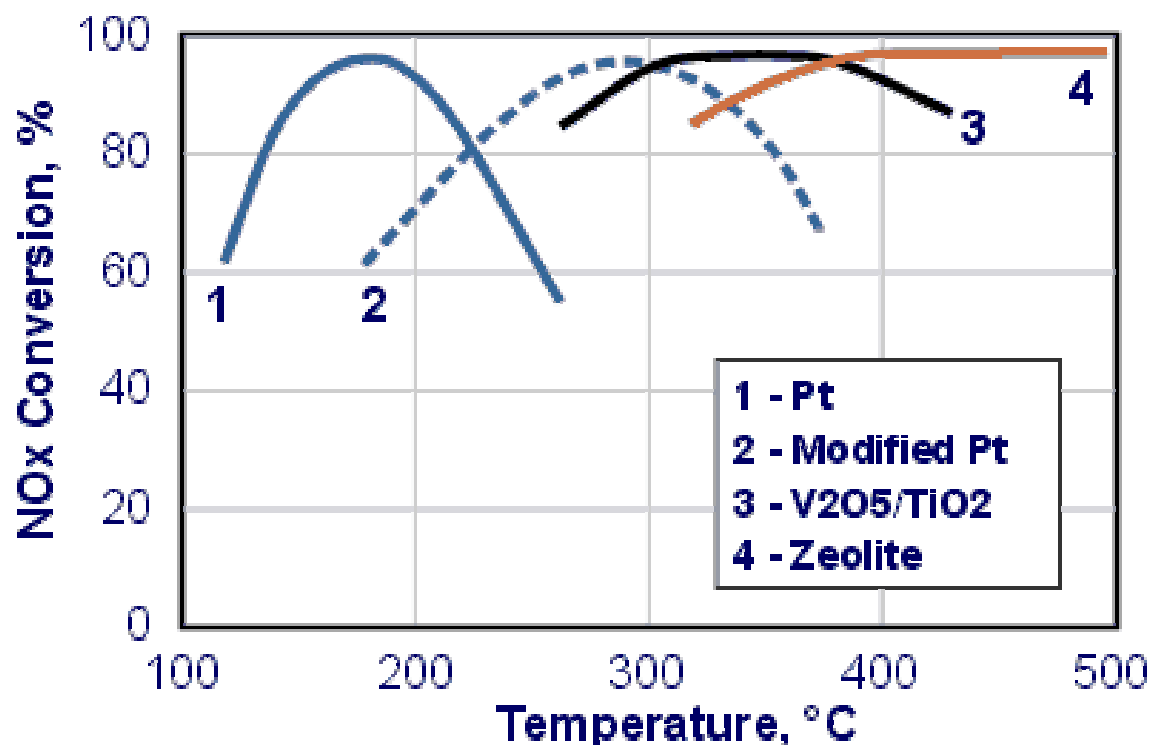
Figure 2-67. Operating temperature windows for different SCR catalysts.

Table 2-14. SCR catalyst technologies.

Catalyst	Temperature Range, °C
Platinum (Pt)	175 – 250
Vanadium (V_2O_5)	300 – 450
Zeolite	350 - 600*

* - ion-exchanged zeolites of greatly improved low temperature activity have been developed for mobile applications

Pt Catalysts: At low temperatures, the SCR reactions, Equation (1) to Equation (5), dominate over the Pt catalyst, so NO_x conversion increases with increasing temperature as shown in Figure 2-67. At about 225-250°C, the oxidation of NH_3 to NO_x and H_2O, Equation (8), becomes dominant. As a result, the conversion versus temperature plot reaches a maximum and begins to fall. To utilize the Pt-based catalyst, one must control the process gas temperature to be above approximately 200°C to avoid NH_4NO_3 formation, Equation (9), but not to exceed about 225°C, where the catalyst loses its selectivity toward the NO_x reduction reaction. This narrow window for temperature control adds expense and complexity to the overall process design. Consequently, this technology is not commonly used today.

Vanadia/Titania Catalysts: Medium temperature V_2O_5 based catalysts operate best in the temperature range between 260 and 450°C. This has the obvious advantage of a wider temperature window than Pt. However, it also exhibits a maximum followed by a decline in NO_x conversion where the catalyst loses activity, as shown in Figure 2-67. NO_x conversion initiates at about 225°C, rises to a plateau at about 400°C, and then falls as the rate of ammonia oxidation begins to dominate. According to Figure 2-67, the selectivity is lost above

about 425°C. The catalyst operating window of newer formulations (Figure 2-68) extends up to about 500°C.

If the exposure temperature of the V_2O_5/TiO_2 catalyst exceeds a certain level, the active, high surface area anatase phase of TiO_2 irreversibly converts to rutile with a surface area of less than 10 m^2/g. Normally, this conversion takes place at about 500 - 550°C, but catalysts may include stabilizers to increase their thermal durability. Tungsten trioxide (WO_3) is the most frequently used stabilizer for SCR vanadia/titania formulations. $V_2O_5/WO_3/TiO_2$ systems became a very common SCR catalyst for both stationary and mobile sources.[131,133]

Stabilized V_2O_5/TiO_2 catalysts were reported to be thermally stable up to 700°C. Example data for such catalyst, showing a dramatic loss of activity after aging at 750°C, is presented in Figure 2-68.[131]
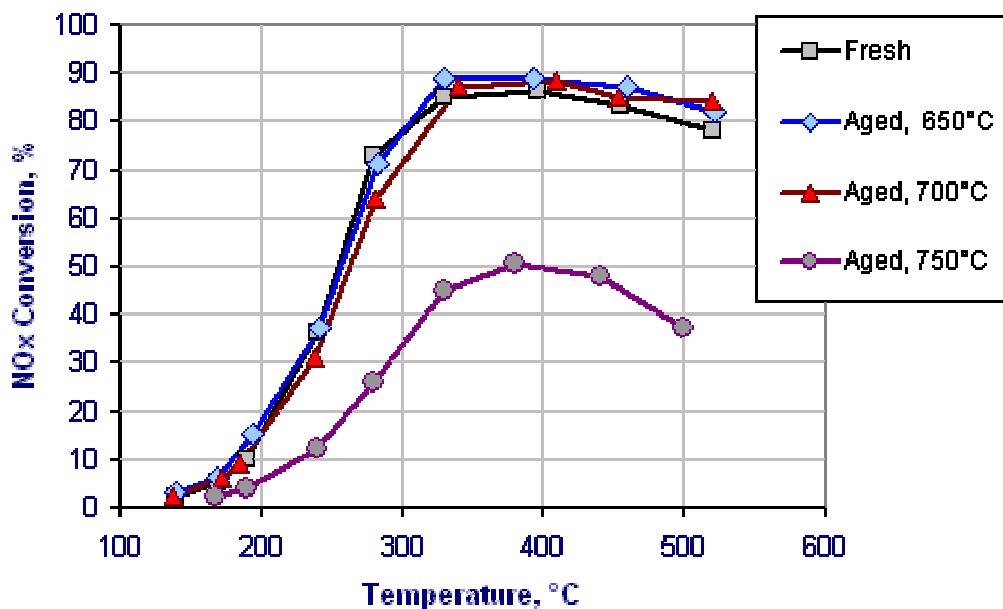
Figure 2-68. Thermal aging of $V_2O_5/WO_3/TIO_2$ catalyst.
(100 hours furnace aging in 10% H_2O, 20 ppm SO_2, air).

Zeolite Catalysts: The first zeolite identified as an active SCR catalyst was mordenite. Common mordenites have a well defined crystalline structure with SiO_2 : Al_2O_3 ratio of about 10. Manufacturers usually do not disclose the precise chemical composition of the zeolites, so it is not possible to describe them in detail. Zeolite SCR catalysts which are commercially available for stationary engines can operate at temperatures as high as 600°C. When NO_x is present, this catalyst does not oxidize ammonia to NO_x according to Equation (8). Therefore, unlike the Pt and V_2O_5 catalysts, its selectivity towards NO_x conversion continually increases with temperature as shown in Figure 2-67.

Zeolite-based catalysts may be prone to stability problems when exposed to high temperatures in the presence of water vapor. At exposure temperatures above 600°C, in a high water content process stream, zeolites tend to deactivate by *de-alumination* whereby the Al^{+3} ion in the SiO_2 - Al_2O_3 framework migrates out of the structure. This leads to permanent deactivation and, in extreme cases, collapse of the crystalline structure.

A different type of a "low temperature" zeolite catalyst has been developed for mobile engine applications.[134,135] A starting point for this formulation was the Cu-exchanged ZSM5 zeolite, well known from the extensive lean-NO_x catalyst research conducted in the 1990's. When used as an SCR catalyst, the Cu/ZSM5 was active in reducing NO_x within the temperature range of about 200-400°C, but its thermal durability was insufficient. New formulations were developed by modifying and ion-exchanging the zeolite with various undisclosed transition metals. The final "low temperature" zeolite catalyst was thermally stable up to 650°C. The normal NO_x reducing activity of this catalyst was low. The formulation has been specifically designed for operation in nitrogen dioxide containing gases, which significantly improved its NO_x conversion and extended the temperature window. In the presence of NO_2, the catalyst yielded better than 90 percent NO_x reduction over the 150-500°C temperature range.

Impact of NO_2 on SCR Catalysis: SCR catalysts used for mobile sources are derived from those used in stationary applications, with the V_2O_5/TiO_2 catalyst being the formulation of choice. Operating temperature windows of these catalysts of about 250-450°C provide the best match with temperatures found in the diesel exhaust. Their low temperature activity, however, is insufficient for diesel engines operated at low loads. The low temperature performance of the catalyst may be increased by using more catalyst volume or by increasing the NO_2 content in the exhaust gas.

Engine-out NO_x emissions are composed in over 90 percent of NO and only in a few percent of NO_2. It was discovered that increasing the NO_2 fraction in the feed gas can improve low temperature activity of the V_2O_5, as illustrated in Figure 2-69. [136] A similar performance enhancement was observed with the Cu/ZSM5 and other "low temperature" zeolite catalysts.[134]
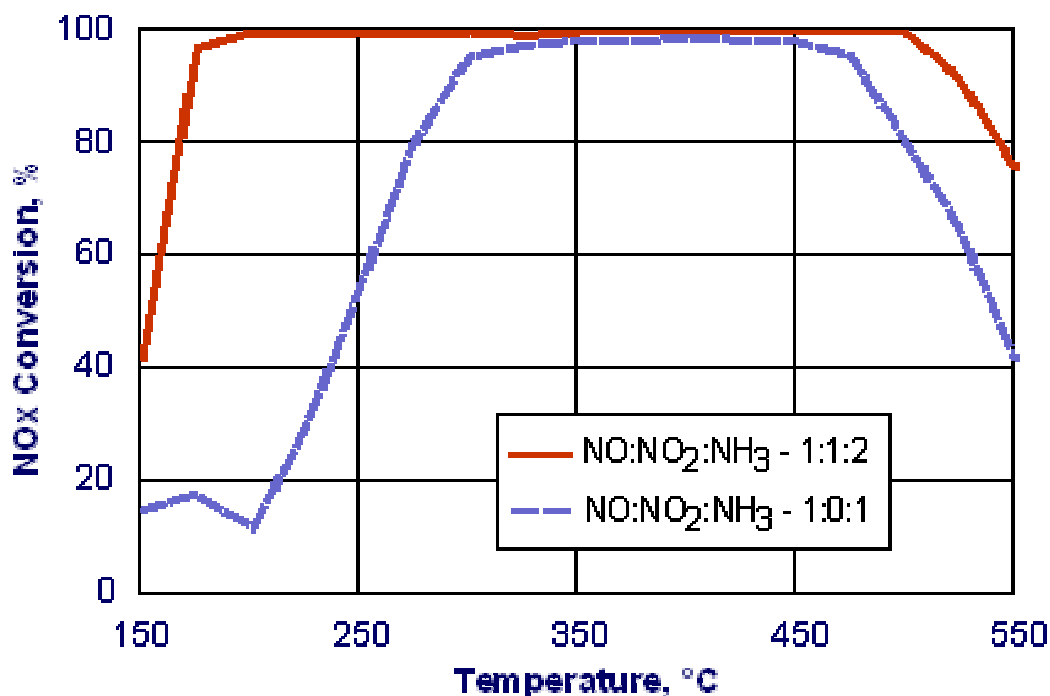
Figure 2-69. Effect of NO_2/NO ratio on NO_X conversion in V_2O_5/TiO_2 catalyst.

The optimum NO_2 content was reported to be 50 percent.[131] At higher contents NO_x conversion efficiency decreases, due to the increased ammonia demand resulting from the substitution of NO by NO_2 [Equations (2) and (3)]. Increased NO_2 levels can be realized in practical installations by an oxidation catalyst that promotes oxidation of NO. The oxidation catalyst should be placed upstream of the urea injection point. Using an oxidation catalyst, the light-off temperature of V_2O_5 catalysts can be decreased to as low as 150°C. Drawbacks of the pre-oxidation catalyst are (1) increased oxidation of sulfur dioxide and sulfate PM make with fuels of higher sulfur content and (2) increased make of nitrate PM.

NO_x conversion in the V_2O_5 SCR catalyst can be also impaired by hydrocarbons, as illustrated in Figure 2-70. In these results, generated with laboratory model gas, an increase in concentrations of n-decane caused increased light-off temperatures for NO_x. An oxidation catalyst placed upstream of the SCR system can also remove hydrocarbons from the exhaust gas, further improving system performance.
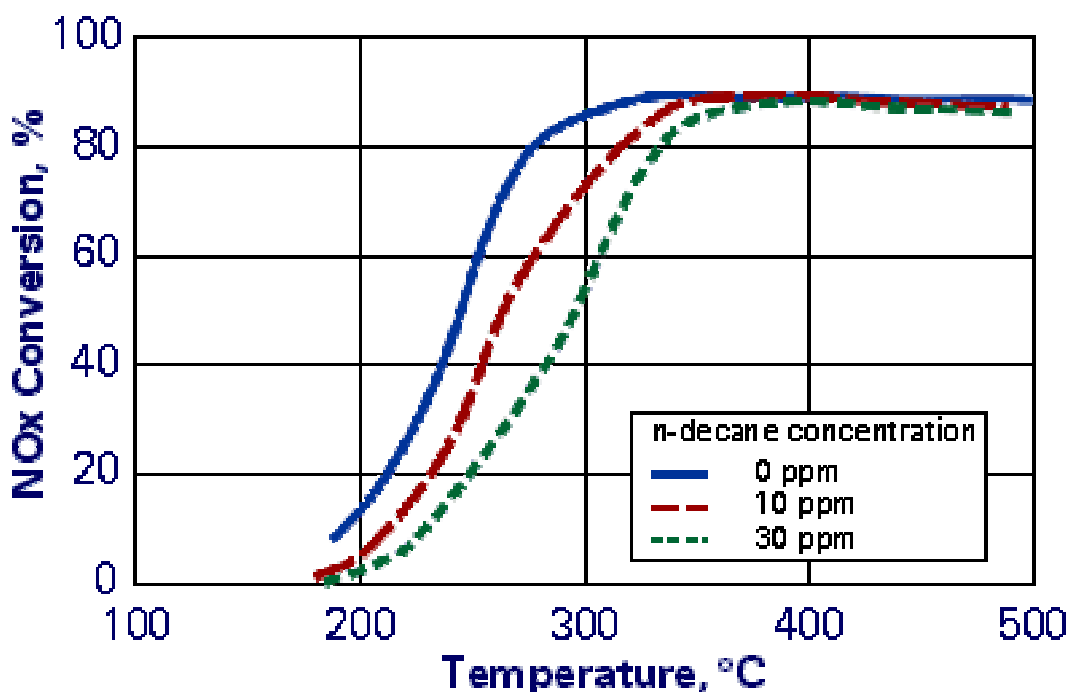
Figure 2-70. Effect of hydrocarbons on NOx conversion in V_2O_5/TIO_2 catalyst.

The pre-oxidation catalyst, similar to that used in the CRT particulate filter, is optimized for high NO_2 generation through the use of high loadings of noble metals. In one engine study, a 2 liter catalyst of 90 g/ft^3 Pt loading was used on a 4.0 liter DI TCI engine.[134]

Auxiliary Catalysts: As mentioned before, SCR systems may also include an oxidation catalyst downstream of the SCR catalyst to control the ammonia slip. It is a typical Pt/Al_2O_3 oxidation catalyst, similar in size to the pre-oxidation catalyst, but of low metal loading, which was reported by some studies at 10 g/ft^3.[134]

Some SCR systems use a dedicated urea hydrolysis catalyst, positioned upstream of the SCR catalyst. The urea hydrolysis catalyst is typically a base metal oxide formulation. For example, Eberhard and co-workers disclosed a mixture of TiO_2 at 110 g/l, Al_2O_3 at 30 g/l, and SiO_2 at 10 g/l, coated on a 150 cpsi substrate, and sized at a space velocity of 90,000 1/h.[125]

Stationary SCR Systems: SCR catalysts for industrial applications can be prepared in a number of different geometric structures. Some are extruded into pellets or homogeneous monoliths, others are supported on parallel metal plates or ceramic honeycomb structures, and still others are fixed on a wire mesh. The appropriate structure depends on the particular application. SCR systems used for NO_x abatement from diesel engines typically utilize monolithic catalysts, which can be either homogeneous or supported on ceramic substrates. Square catalyst modules are usually assembled into layers (baskets), which in turn fit into the steel catalyst housing. The principal SCR suppliers and the catalyst types are identified in Table 2-15.[120,130]

Table 2-15. Suppliers of industrial SCR catalysts.

Supplier	Catalyst Type	Operating Temperature, °C
Japan		
Babcock Hitachi	Base metal/metallic substrate	250 - 416
Hitachi Zosen	Base metal/ceramic monolith or wire mesh	330 - 421
Ishikawajima-Harima Heavy Industries	Base metal/ceramic monolith	204 - 400
Kawasaki Heavy Industries	Base metal/ceramic monolith	300 - 400
Mitsubishi Heavy Industries	Base metal/ceramic monolith	204 - 400
UBE	Base metal/ceramic monolith	250 - 400
U.S.		
W.R. Grace	Noble metal/metallic substrate	225 - 275
Engelhard	Base metal/ceramic monolith	302 - 400
Johnson Matthey	Base metal/metallic substrate	343 - 427
Norton	Zeolite	221 - 521
Europe		
BASF	V_2O_5-TiO_2-WO_3/homogeneous monolith	-
Siemens	V_2O_5-TiO_2-WO_3/homogeneous monolith	-
Steuler	Zeolite	300 - 521
Haldor Topsoe	V_2O_5-TiO_2/homogeneous monolith	-

Cell densities in monolithic SCR catalysts vary from less than 10 cpsi to 200 cpsi. The smaller cells (larger cell densities) are used for clean gas applications and larger cells for "dirty" gas applications. Units with large cells are usually very large. The process gas space velocities can be as low as 3,000 to 5,000 1/hr. Small cell substrates, such as 200 cpsi, are usually sized for space velocities of 10,000 to 20,000 1/hr, but sometimes as high as 40,000 1/hr.

Most stationary SCR systems use ammonia as the reducing agent. However, since the late 1980's, urea based systems have been increasingly popular. The traditional method of injecting ammonia into the exhaust gas stream utilizes pure *anhydrous ammonia*. Liquid ammonia is stored in a pressurized tank. From there it is piped to a heater (typically an electric heater), where the liquid vaporizes. The ammonia vapor is next routed into a mixing chamber, where it mixes with ambient air supplied by a fan or blower in a predetermined ratio. The ammonia-air mixture is then directed to the distribution grid system for subsequent injection into the flue gas stream at a location upstream of the SCR reactor. The NO_x concentration downstream of the reactor is used as a feedback to control the amount of injected ammonia. A precise ammonia injection control is essential to obtain high NO_x conversion and low ammonia slip.

An alternative approach for ammonia injection is the use of *aqueous ammonia*, $NH_3 \cdot H_2O$, which has lower vapor pressure, is easier to handle, and is less hazardous. A schematic of an aqueous ammonia injection system is shown in Figure 2-71.[121] It contains two trains of piping, one for aqueous ammonia and the other for carrier air, which feed into a vaporizer. Aqueous ammonia is stored at ordinary temperature in a tank. From there it is pumped, filtered, metered, and sprayed through atomizing nozzles into the vaporizer. In the vaporizer ammonia is evaporated by mixing with hot air. Ambient air is drawn by a blower and heated, then enters the vaporizer through nozzles at the top of the vessel.
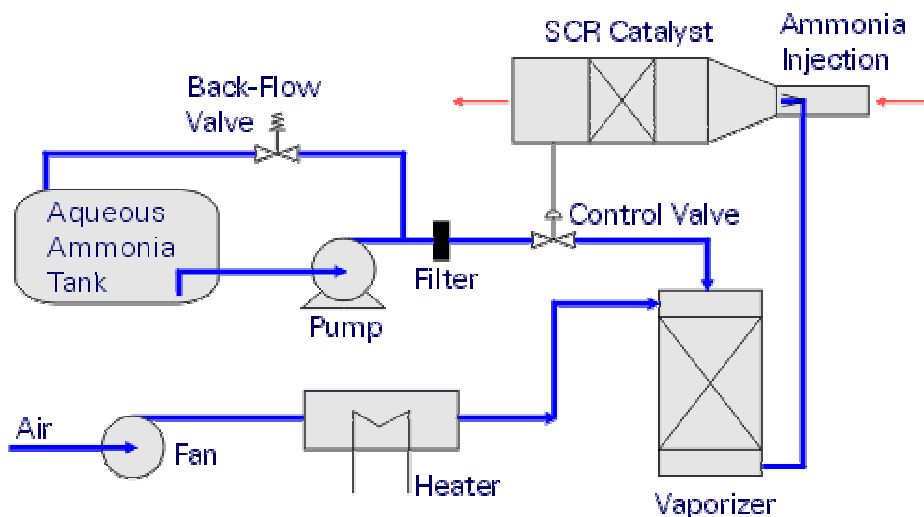
Figure 2-71. Aqueous ammonia injection system.

The air heater is usually electric, but heating coils placed directly in the process gas or heated by steam can also be used. The vaporizer is a column apparatus, usually packed with metallic rings or other packing to promote the mixing and evaporation processes. The mixture of ammonia, air and water vapor is then injected into the flue gas stream. It is important to obtain a homogeneous NH_3/NO_x ratio in the entire process gas stream. The injection grid network consists of a number of pipes connected in parallel, each of which contains several orifice holes. The pipes and holes are sized to provide balanced ammonia flow distribution throughout the process gas. A static mixer may be placed in the exhaust duct to further improve mixing.

Stationary SCR systems often feature a closed-loop control system. The concentration of NO_x and/or NH_3 in the exhaust gas is continuously monitored and used as a feedback signal to control the amount of ammonia/urea to be injected.

SCR Systems for Mobile Engines: At this time, SCR remains the only proven catalyst technology which is capable of reducing diesel NO_x emissions to levels required by future emission regulations. The use of ammonia has been practically ruled out, due to safety concerns, and urea is the reductant of choice. Most development work is currently targeting the heavy-duty Euro V (2008) standard of 2 g/kWh NO_x. SCR is envisioned as one of the most promising technologies to simultaneously meet the Euro V limits for both NO_x and for PM.[137] It is possible to calibrate heavy-duty engines for very low particulate emissions, below the Euro V limit of 0.02 g/kWh. Such low PM engine calibration leads to higher NO_x emissions; a worst case baseline NO_x of 7-8 g/kWh may be increased to some 9-11 g/kWh. A urea-SCR aftertreatment system can then be used to bring down the NO_x emissions to below 2 g/kWh. The required reducing capacity of the SCR system of about 80-85 percent is believed to be technically feasible. SCR systems of reduction efficiencies in this range have been already demonstrated.[137] The need for a separate diesel particulate filter is eliminated in this strategy, resulting in smaller size, complexity, and cost of the overall emission aftertreatment system.

SCR systems are also being developed for a number of other applications, including light-duty (both in the EU and the U.S.) and the US 2007 heavy-duty NO_x standard of 0.2 g/bhp-hr. This standard is much more stringent compared to the Euro V. Relative to the 2002/2004 standards, which can be met by the cooled EGR technology, an over 90 percent NO_x reduction over the transient FTP test is necessary; SCR systems of such performance have not yet been demonstrated, but their development is in progress.[138]

Calibrating engines for low PM and high NO_x involves advanced injection timing, resulting in improved fuel economy.137The "Euro V calibration" mentioned above brings an estimated 3-5 percent fuel saving over the regular engine calibration. Some authors conclude that these fuel savings would provide a quick payback for the cost of the SCR system. One needs to be skeptical and carefully verify such claims. In general, the potential savings depend on the fuel costs and driving distances that vary in different geographical areas. The fuel savings are also directly off-set by the cost of urea, which is consumed at about 3 percent of the fuel volume. Finally, in applications where stringent NO_x standards are in place, the SCR technology may have little or no extra capacity to handle the additional engine-out NO_x levels which result from fuel efficient engine calibration.

Depending on the particular application and NO_x reduction requirement, the application of SCR technology to mobile engines still remains a challenging task which requires solving a number of technical, regulatory, and urea distribution-related problems. The following are the most important issues:

-   **Catalyst selection and system configuration**: Most stationary applications, both industrial and diesel engines, are characterized by steady-state operating conditions. Mobile diesel engines, on the other hand, operate under transient duty cycles with great variation of mass flow, exhaust temperature, and NO_x concentration. The catalyst has to operate under a much wider temperature window than in stationary

applications. In addition, the transient operation presents challenges in the development of urea injection strategy, makes it more difficult to control the formation of secondary emissions (NH_3, N_2O, NH_4NO_3, ...), and to achieve required catalyst durability.

-   **Size, complexity, and cost of SCR systems:** SCR catalysts are much larger than those used by other catalyst technologies. Most proposed systems also include auxiliary catalysts to enhance the performance of the SCR catalyst and/or to control ammonia slip. In addition, a complex reductant injection/control system and on-board storage capacity are needed. All this translates to expected high costs of SCR systems.

-   **Regulatory compliance and urea distribution issues:** The diesel engine can run without the reductant. Since there is no incentive to the vehicle operator to replenish used reductant, regulatory authorities are concerned that vehicles may be operated without urea making SCR systems inactive.

-   **Other problems:** include the lack of distribution infrastructure and freezing of urea solutions in winter.

Experience

Not surprisingly, first mobile SCR NO_x control systems were installed on marine applications. Large sizes and steady-state operation of marine units, similar to stationary diesel engines, make the adaptation of stationary SCR technology straightforward. The first SCR units were installed in 1989 and 1990 on two Korean 30,000 metric ton carriers. The ship operator was seeking a permit from the Bay Area Air Quality Management District (BAAQMD) to allow the reduced-emission ships in its docks. Both ships were powered by MAN B&W 2-stroke 8 MW diesel engines. The ships were equipped with ammonia SCR system designed for 92 percent NO_x reduction. The SCR reactor included a by-pass system. Exhaust gases were passed through the reactor only when the ships were sailing in waters subject to NO_x emission regulations.

Commercial SCR systems have been also installed on ferries. In 1992 the ferry "Aurora of Helsingborg" that shuttled between Sweden and Denmark was equipped with a urea SCR system.[130] The engine was 2.4 MW Wartsila, type 6R32E. The reactor included three layers of monolithic extruded SCR catalysts and one layer of an oxidation catalyst.

The SCR technology has also been considered for NO_x control from locomotive diesel engines.[139] Numerous development projects aimed at adapting SCR technology to diesel powered truck and car engines have been conducted in Europe and the U. S. A. In a project sponsored by the Netherlands Ministry of Environment, a 12 liter heavy-duty diesel engine equipped with an urea SCR catalyst system was tested under both steady-state and transient conditions.[140,141] In another study by FEV and Ford a urea SCR system was tested on a 2.5 liter light-duty diesel engine.[142] TNO Automotive and Engelhard have developed an SCR system for heavy-duty engines, which was tested on DAF and Renault trucks.[143]

Not surprisingly, mobile systems have been also developed by companies with traditional expertise in stationary installations, such as Haldor Topsoe[144] or Siemens with its automotive SCR system termed SiNOx. Reported SiNOx demonstration programs involved bench testing, chassis dynamometer tests, and vehicle road test with a number of heavy-duty trucks which were operated by trucking companies in regular duty.[127] A prototype of the Siemens system has also been tested on a heavy-duty truck on US highways as well as at SwRI on behalf of the Manufacturers of Emissions Control Association (MECA 1998).[128]

System Configuration: Final configuration of an SCR system for mobile engines has not yet been established. There are a number of differences between systems proposed by different developers and systems evolve with time. The general layout shown in Figure 2-72 combines a number of features from different SCR systems. Since suitable, fast response NO_x or NH_3 sensors are not available, the outlet exhaust gas concentration cannot be used as feedback for the process control. Instead, the SCR systems for mobile engines work in an open loop configuration where a pre-programmed map of engine NO_x emissions is used to control the urea injection rate as a function of engine speed and load. This open loop configuration is capable of some 80 percent NO_x reductions, as required for heavy-duty Euro V applications. However, closed loop systems are likely to be required for more demanding applications of 90 percent+ NO_x reduction targets. It was estimated that SCR systems to meet the US2007 standards would require NO_x sensors of 40-20 ppm NO_x sensitivity and little cross-sensitivity to NH_3.[138] The use of closed loop systems would also minimize the amount of engine calibration work that is required in the development of open loop systems.
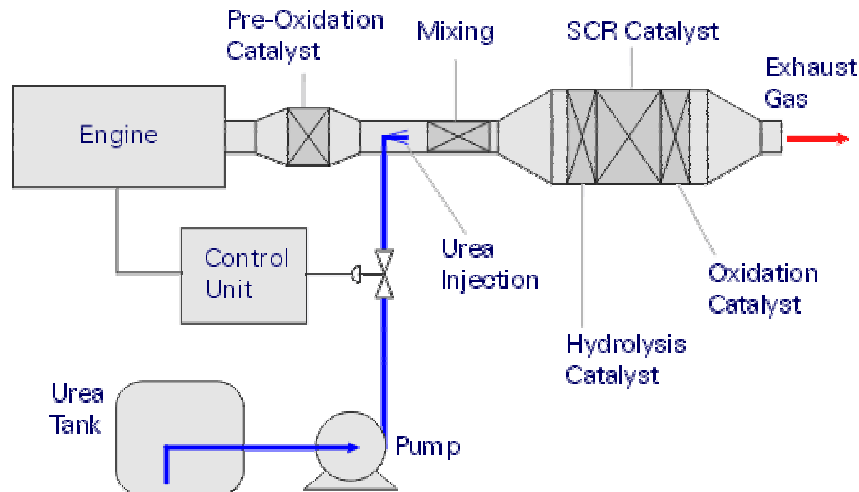
Figure 2-72. Open loop urea SCR system for mobile diesel engines.

The urea solution is pumped from the urea tank and sprayed through an atomizing nozzle into the exhaust gas stream. Thorough mixing of urea with exhaust gases and uniform flow distribution are important in achieving high NO_x conversions.[145] In addition, static mixing devices may be provided downstream, as well as upstream (not shown in Figure 2-72), of the urea injection point.[146] In some systems used for marine engines urea was first mixed with air, supplied by a dedicated fan. A similar injection system supplying urea aerosol has been designed for trucks, utilizing compressed air from the vehicle's suspension system.[143] Regardless of the injection method, it must be emphasized that optimization of the urea

injection process, in terms of accuracy and reproducibility, is one of the most important areas where SCR performance improvement can be achieved.

Once mixed with the hot exhaust gas, the urea undergoes hydrolysis and thermal decomposition producing ammonia. In some systems the urea hydrolysis is additionally promoted by a dedicated hydrolysis catalyst installed upstream of the SCR catalyst.[131] In most systems, however, the SCR catalyst itself promotes both urea hydrolysis and the SCR reaction.

The mixture of exhaust gases and ammonia (decomposed urea) enters the SCR catalyst where nitrogen oxides are reduced to nitrogen. SCR catalysts for mobile applications have been using both coated metallic/ceramic substrates and homogeneous V_2O_5/TiO_2 extrusions, which were developed for stationary applications. Homogeneous catalysts of corrugated construction with cell densities as high as 300 cpsi were also developed.[137] Reducing the catalyst size is one of the major objectives of ongoing development. The exhaust gas space velocities in the first mobile SCR catalysts were typically between 20,000 and 30,000 1/hr. Lower space velocities provided higher NO_x reductions and lower ammonia slip, but resulted in large catalyst sizes. In one of the early SCR projects, a 12 liter heavy-duty diesel engine was equipped with 70 liters of catalyst volume at a space velocity of 21,500 1/hr.[140]

Catalyst volume reductions can be achieved by optimization of its geometry, such as increasing the cell density. Coated SCR catalysts can have cell densities up to 400 cpsi,[143] matching those used in other diesel catalyst technologies. Homogeneous catalysts become available with gradually increasing cell density. For example, an increase in the cell density of the SiNOx homogeneous extrusion from 100 to 200 cpsi allowed reducing the catalyst volume on a 12 liter heavy-duty engine from 63 to 45 liters.[128] Further significant catalyst size reductions may be realized by installing a pre-oxidation catalyst, designed to generate NO_2 and remove hydrocarbons, upstream of the urea injection point. In one of the studies that used precatalysts, SCR catalysts volumes of 4.6 - 9.2 liters were tested on a 4.0 liter heavy-duty engine.[131] The volume of the pre-catalyst was 2 liters. In another study, also utilizing pre-catalysts, the volume of a homogeneous SCR catalyst was reduced to about 20 liters on a 12 liter, 400 hp engine by increasing the cell density to 300 cpsi.[137]

Many systems include an oxidation catalyst positioned downstream of the SCR catalyst. The volume of this catalyst is comparable to that of the NO_2 pre-catalyst, but the noble metal loadings are much lower (one study reported 10 g/ft^3 Pt compared to 90 g/ft^3 Pt in the pre-catalyst.[137] The function of this "cleanup catalyst" is to oxidize ammonia slip that may appear due to the imperfect control strategy or in case of SCR catalyst failure. An added benefit of the oxidation catalyst is the control of hydrocarbons and carbon monoxide emissions, as well as the diesel odor. Disadvantages of the ammonia slip catalyst include (1) increased proportion of nitrous oxide, N_2O in the exhaust gases[147] and (2) increased NO, both generated though the oxidation of ammonia according to Equation (6) and (8), respectively. The oxidation of NH_3 to NO may cause an apparent decrease of NO_x conversion efficiency in SCR systems equipped with ammonia slip catalysts at higher exhaust temperatures.[137]

Typically, the urea injection controller also monitors the exhaust gas temperature. When the temperature drops below a predetermined value, somewhere between 150 and 300°C

depending on the catalyst type and configuration, the controller closes the urea supply to prevent catalyst deactivation (e.g., by ammonium sulfate or un-hydrolyzed urea) and secondary emissions that may occur at low temperatures.

An alternative reductant supply approach is to use solid urea rather than water solutions. The advantages of solid urea include (1) less on-vehicle space requirement for storing the reductant (or achieving a higher driving range at a given storage volume), (2) avoiding the exhaust gas cooling effect associated with the evaporation of water, and (3) avoiding the freezing problems in cold climate areas. However, systems proposed for dozing solid urea appear to be more complex than those utilizing solutions. MAN has developed a system utilizing small diameter urea pellets.[125] The system includes a urea pellets container, a motorized feeder, and a grinder. The urea powder produced in the grinder is carried by compressed air to the exhaust system and mixed with exhaust gases in a special mixing chamber upstream of the hydrolysis catalyst. Reported problems included (1) adsorbing atmospheric moisture and forming clusters by the urea pellets, leading to clogging of the dosing system, and (2) corrosion problems by melted urea, requiring either expensive steel grades or protective surface coatings.

Urea Consumption and Replenishment

Most proposed SCR systems require that aqueous urea solution be carried in an on-board storage tank that requires periodic replenishment. Reported SCR developments on light duty engines indicated an average consumption of 2.5 cm^3 of urea solution per km (0.25 l/100 km) on a 2.5 liter diesel engine. At this consumption level, a 40 liter on-board urea tank would have to be re-filled every 15,000 km.[142]

In an SCR demonstration project with a US Class-8 highway truck, diesel fuel and urea consumption were found to be 5.2 mpg (45.2 l/100km) and 94 mpg (2.5 l/100km), respectively. At this rate, a 15 gallon (57 l) urea tank would allow for 1,410 miles (2,260 km) of truck operation between refills. In another heavy-duty engine project, a urea consumption of 3 percent of the fuel by volume (or 4 percent by mass) was reported.[143]

Commercial introduction of SCR systems would require establishing a urea distribution infrastructure. The implementation of such system poses a number of logistics and regulatory emission compliance challenges. Urea solutions would need to be distributed along with the diesel fuel throughout the fuel distribution network. The fueling system should prevent, or at least minimize, the possibility of operating the vehicle with an empty urea tank. "Intelligent", computerized fueling terminals have been proposed, which would communicate with the vehicle's electronic control unit and simultaneously dispense the required amount of fuel and urea through a special dual fueling nozzle.[148,149]

Maintaining the urea infrastructure has also serious economic implications. The infrastructure cost may be in fact the major component of the urea price at the pump, more than off-setting any fuel economy gains due to the use of SCR with fuel efficient engine calibration. A comprehensive urea infrastructure cost analysis was carried out by the U.S. Department of Energy. The costs of producing and distributing urea were estimated separately. Depending on the assumptions (demand, the number of retail points, and the level of product segregation), the distribution cost ranged from $0.70 to $35 per gallon ($0.18 - $9.25 per liter) of 32.5 percent SCR-urea solution. The lower end of the range assumed high throughput truck stops,

while the upper part represented light-duty retail outlets with low throughput of urea. Production costs were estimated to range between $0.12 and $0.30 per gallon ($0.03 - $0.08 per liter), with an estimated $0.05 to $0.10 per gallon ($0.01 - $0.03 per liter) to be added to the cost when urea solution is sold.

Cold temperature properties of urea solutions would also need to be addressed in commercial SCR systems. Since urea solutions have freezing temperatures of -11°C, which is not acceptable for winter conditions in most of Europe or North America, the storage tanks and tubes would need to be heated. Alternatively, additives could be used to lower the crystallization temperature of aqueous urea solutions to acceptable levels below -30°C.

Emission Performance

It has been demonstrated in several studies that the SCR catalyst is capable of efficiently reducing diesel engine NO_x emissions. Reported NO_x conversion efficiencies in heavy-duty engines ranged from about 55 percent to 90 percent, depending on the application and test method.[127,128] Higher conversions are measured on EU steady-state cycles, such as the ESC. The US FTP procedure has been more challenging due to both its transient characteristic, and low exhaust temperatures and low conversions in the initial portion of the test.

It has been convincingly demonstrated that Euro II engines can meet the Euro V NO_x emission standard of 2.0 g/kWh when equipped with SCR systems.[143] As an example, the study of the TNO/Engelhard system on DAF and Renault trucks showed NO_x conversions of 81-84 percent on the ETC test and 72 percent over the ETC test, with almost all results below 2 g/kWh NO_x. These results were achieved through careful optimization of the urea injection. The catalyst system itself was rather simple, with a single SCR catalyst sized at 45,000 1/hr space velocity (34 dm^3 catalyst on 400 cpsi substrate on a 12 liter engine) and no oxidation pre- or ammonia slip catalysts. US 1994 engines can also meet the 2004 NO_x standard utilizing SCR. However, reducing NO_x emissions to 0.2 g/bhp-hr, the US NO_x standard for the year 2007, has not yet been demonstrated. It may quite likely require closed loop SCR controls to become feasible.[138]

In an SCR study with a 2.5 liter light-duty diesel engine, NO_x conversions of up to 60 percent on the ECE+EUDC cycle and up to 83 percent on the FTP-75 cycle were reported.[142] There is also a number of *undesirable emissions* that may be created in SCR catalysts. SCR systems which do not include oxidation catalysts may produce emissions of (1) *ammonia* (ammonia slip) and (2) *ammonium nitrate* particulates. If the system also includes an oxidation catalyst, additional secondary emissions may be produced, such as (3) *sulfate particulates* (ammonium sulfate), and (4) *nitrous oxide*.

Progress made in the ammonia dozing equipment made it possible to lower the ammonia slip in mobile systems to levels almost equivalent to those seen in stationary SCR systems. A number of publications reported ammonia slips of less than 10 ppm. In the TNO/Engelhard system, which did not include an ammonia slip catalyst, an average ammonia slip of 6 ppm and a maximum slip of 37 ppm were measured.[143]

The tendency of the diesel oxidation catalyst to form sulfate emissions is commonly known. It increases with temperature and with sulfur content in the fuel. A 40 percent increase in PM emissions due to the sulfate formation was reported in an SCR/oxidation system on the hot ECE R49 cycle.[141] An increase in PM emissions in an SCR catalyst (in a system which also included an oxidation catalyst) was also reported when using ultra low sulfur fuels.[136] The most likely explanation was a combined effect of sulfate and ammonium nitrate particulate emissions generated in the SCR catalyst. Decreases of total PM emissions (by 4-23 percent) were measured in SCR systems that have not included oxidation catalysts.[143]

Increased emissions of nitrous oxide (N_2O) reported in many publications are specifically related to the ammonia slip in the SCR catalyst. A high proportion of ammonia slip can be converted in the oxidation catalyst to N_2O, according to Equation (6). One study found that proportion to be between 25 and 50 percent of the total ammonia emission.[141] Nitrous oxide levels of 11 to 20 ppm were measured after the oxidation catalyst. It was also found that the engine-out nitrous oxide, of about 3 ppm, was practically unchanged in the SCR catalyst. The N_2O emission could be avoided by the elimination of the oxidation catalyst. In theory this could be achieved through a better urea injection control, preferably in the closed loop configuration, resulting in acceptably low ammonia slip. However, since the oxidation catalyst downstream the SCR catalyst allows a larger $NH_3:NO_x$ window, its elimination in systems of high NO_x reduction requirements may be problematic.

C.6. 2. Diesel Parliculate Filters

Diesel particulate filters are primarily used to reduce PM emissions. The filter typically consists of a ceramic filter that filters, or traps, the exhaust. Eventually, particulate filters require some periodic "cleansing" by either reversing the direction of the exhaust flow, or cleaning the filter in a liquid. Particulate filters may also be "regenerated" to prolong their effective use by burning the trapped PM. There are two methods of regeneration: active and passive. Active regeneration utilizes an external device or event to actively regenerate the filter. The use of external heating elements is an example of an active regeneration method where the heating elements periodically raise the temperature of the filter to burn the trapped PM. A passive regeneration system typically uses filters that are coated with a catalyst material. The catalyst provides a catalytic reaction to lower the combustion temperature required to burn the trapped PM. Consequently, exhaust temperatures normally occurring in MDDEs and HDDEs may be suitable to burn most of the PM emissions. Further, there is also a reduction in hydrocarbon and carbon monoxide emissions.

A variation to the catalyzed particulate filter is the use of fuel borne catalysts. Rather than coating the filter with the catalyst, a small percentage of catalyst solution is mixed into the fuel. Since the catalyst is present in the combustion chamber, the catalyst also immediately becomes a component of the exhaust and the catalytic reaction begins earlier. By using the fuel borne catalyst in conjunction with the catalyzed diesel particulate filter a better reduction of PM emissions compared to use of a catalyzed diesel particulate filter alone.

Diesel particulate filters have been proven successful in a variety of worldwide applications and demonstration programs. Though some failures have occurred, they mainly involved later model engines and engines using diesel fuel with a high sulfur content. For catalyzed particulate traps, high fuel sulfur content results in high levels of sulfate-based PM, making

low "tail pipe" PM levels infeasible. Recent tests using diesel particulate filters have demonstrated a reduction of PM emissions by 90 percent and more.

C.6.2.1. Catalyzed Diesel Filters

Most catalyzed diesel filters utilize monolithic wall-flow substrates coated with a catalyst. The catalyst lowers the soot combustion temperature, allowing the filter to self-regenerate during periods of high exhaust gas temperature. A number of diesel filter catalysts have been developed, including both noble and base metal formulations. Catalyzed ceramic traps exhibit very good PM filtration efficiencies, but are characterized by relatively high exhaust gas pressure drop.

Application of a catalyst has been attempted with virtually all diesel filter media in order to develop passive trap systems. The function of the catalyst in the catalyzed diesel particulate filter (CDPF) is to lower the soot combustion temperature to facilitate regeneration of the filter by oxidation of diesel particulate matter (PM) under exhaust temperatures experienced during regular operation of the engine/vehicle, typically in the 300-400°C range. In the absence of the catalyst, PM can be oxidized at appreciable rates at temperatures in excess of 500°C, which are rarely seen in diesel engines during real-life operation. Reported catalyst applications include cordierite and silicon carbide wall-flow monoliths, wire mesh, ceramic foams, ceramic fiber media, and more. The most common type of a CDPF is the catalyzed ceramic wall-flow monolith.

Catalyzed ceramic traps were developed in early 1980's. Their first applications included diesel powered cars and, later, underground mining machinery. Catalyzed filters were commercially introduced for Mercedes cars sold in California in 1985. Mercedes models 300SD and 300D with turbocharged engines were equipped with 5.66" diameter $\times$ 6" filters, Figure 2-73, fitted between the engine and the turbocharger.[150]

Figure 2-73. Catalyzed soot filter for Mercedes Benz 300d.

The use of diesel traps on cars was later abandoned, due to such issues as insufficient durability, increased pressure drop, and filter clogging. Today, even though not all of these problems have been solved, catalyzed ceramic traps remain one of the most important diesel filter technologies. CDPFs are increasingly used in a number of heavy-duty applications, such as urban buses and municipal diesel trucks. For a number of years, limited quantities of catalyzed filters have been also used in underground mining (North America, Australia) and in certain stationary engine applications.

Catalyzed ceramic filters are commercially available for a number of highway, off-road, and stationary engine applications as both OEM and aftermarket (retrofit) product. The list of suppliers includes Engelhard, OMG dmc[2], as well as several smaller emission control manufacturers who specialize primarily in the off-road markets.

C.6.2.2. Catalyzed Diesel Filter Design

A schematic of a catalyzed ceramic diesel filter is shown Figure 2-74. The main component of the filter is a ceramic (cordierite, SiC) wall-flow monolith. The porous walls of the monolith are coated with an active catalyst. As the diesel exhaust aerosol permeates through the walls, the soot particles are deposited within the wall pore network, as well as over the inlet channel surface. The catalyst, through a number of possible mechanisms discussed below, facilitates PM oxidation by the oxygen present in exhaust gas.
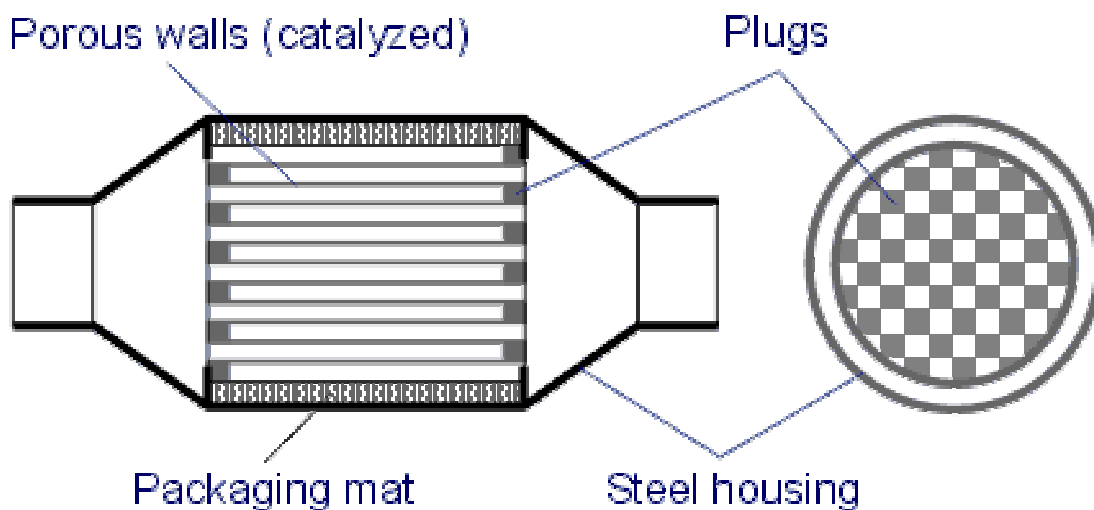
Figure 2-74. Schematic representation of wall-flow filter.

The ceramic monolith is packaged into steel housing. Typical wall-flow monolith packaging techniques are used. To minimize the total exhaust system back pressure, soot filters are usually installed without mufflers. Wall flow monoliths have their own noise attenuation properties and are in most cases a sufficient replacement for the muffler. To minimize installation costs, filter housing may be designed as a direct-fit replacement of the vehicle muffler. Such CDPF-muffler design is common in retrofit urban bus applications.

Since the filter regeneration critically depends on high temperatures, the unit should be installed as close to the engine exhaust manifold as possible. To further prevent heat losses,

thermal insulation of the filter and the inlet exhaust piping is often provided. Typically, insulation can prevent about 10°C or more temperature decrease per 1 m of exhaust pipe length due to heat losses. In OEM applications, where the filter system can be fully integrated with the engine, the pre-turbo position of the particulate filter would provide exposure to the highest possible exhaust temperatures.

Catalyzed filter sizing varies greatly, depending on the engine technology, duty cycle, fuel quality, and other factors. The most important parameter affecting the filter sizing is the engine-out PM emission, which influences both the regeneration process itself, and the soot holding capacity requirement of the filter. Old, high PM-emission engines typically require much larger filter sizes than cleaner engines. Approximate filter sizing rules depending on engine technology are listed in Table 2-16. The numbers listed under high PM engine category roughly corresponds to filter sizing used for older, mechanical engines in underground mine applications. The sizing rules given for low PM emission engines describe the smallest filter volumes as used in certain US-1994 compliant or better highway engines.

Table 2-16. Typical CDPF sizing ranges in heavy-duty engines*.

Parameter	Engine PM Emission	
	Low (≤0.05 g/bhp-hr)	High (≥0.30 g/bhp-hr)
Space velocity, 1/h	80,000	25,000
Filter volume/engine displacement ratio	1.5	4
Filter volume/engine rated power, cm^3/hp	40	150

* - Based on 100/17 wall-flow monolith geometry. Smaller filter sizes may be sufficient if monoliths of higher specific filtration surface area are used.

C.6.2.3. DPF Catalyst Systems

Various catalyst systems used for diesel filters utilize noble metals, base metals, as well as mixtures of noble and base metals. Platinum is the most active and the most commonly used noble metal, but palladium, rhodium or ruthenium catalysts, usually in mixtures, are also possible. The list of common non platinum-group metals used in diesel filters includes vanadium, magnesium, calcium, strontium, barium, copper and silver.

The most convenient method of applying catalyst to the ceramic monolith is impregnation with water-based solutions of catalyst precursors, followed by drying and calcining. The final catalyst (usually metal or metal oxide) is formed from the precursor at elevated temperatures during the calcining process. Working with water solutions provides a uniform distribution of the catalyst throughout the porous filter walls. Some diesel filter catalysts are also applied from water suspensions of insoluble oxides or salts. Several formulations containing vanadium are examples of catalysts applied from suspensions.[151,152] Whenever suspensions are used, the particle size distribution of the suspended material, as well as other process parameters, must be carefully controlled to prevent clogging of the filter pores with the catalyst. This is especially important for newer ceramic monolith materials that are characterized by much smaller pore diameters (about 10 μm) than those used in the past.

Platinum group metals, including platinum and palladium, are compatible with *cordierite* and can be applied to ceramic monoliths without a transition metal oxide carrier or washcoat layer. Although various catalyst carriers, such as alumina, silica and zirconia, have been suggested,[153] most of today's diesel filters do not include a high surface area catalyst carrier. Application of the transition oxide catalyst carriers or, even more so, a washcoat layer to filter monoliths of small pore diameters is very problematic. The resulting "carrier-less" diesel filter catalysts, however, have very low physical surface area, resulting in poor catalyst dispersion. Theoretically, such catalysts should be troubled by a number of durability problems, including sintering or reactions between the catalytic components and the ceramic substrate. The published data is still insufficient to determine if such phenomena indeed happen in catalyzed soot filters.

Even less experience exists with catalytic coating of *SiC* filter substrates. The surface of silicon carbide grains that form the wall-flow monolith has a very smooth, almost glossy appearance that appears to be incompatible with catalysts. Several authors suggested applying some kind of intermediate oxide layer composed of alumina or zirconia - alumina before applying platinum group catalysts on SiC parts.[154,155] For some oxides, it is possible to apply such intermediate layer through impregnation using water-based precursors and, thus, avoiding the inconvenient washcoat (i.e., suspension-based) technologies.

Noble Metal Catalysts: The most common noble metal catalyst used in diesel filters contains platinum with promoters, such as alkaline earths. Typical platinum loadings in filters used for off-road engines through the 1990's were between 35 and 50 g/ft^3. These filters, installed on relatively high polluting engines, required minimum temperatures of nearly 400°C for regeneration. Later, when catalyzed filters were applied to much cleaner urban bus and other highway vehicle engines, it was found that they were able to regenerate at much lower temperatures. However, higher platinum loadings were needed to support the low temperature regeneration. Filters used in clean engine, low temperature applications have typically platinum loadings of 50-75 g/ft^3.

An example platinum catalyst developed by Engelhard is composed of 5-150 g/ft^3 Pt/Rh at 5:1 ratio and 30-1500 g/ft^3 of MgO. The catalyst is impregnated onto cordierite monoliths from water based solutions. A filter coated with the catalyst requires exhaust temperatures of 375-400°C to regenerate. The function of rhodium in the above formulation is to suppress the catalytic oxidation of SO_2 and, thus, the sulfate make in the catalyst. The final effect depends on the Pt/Rh ratio. Table 2-17 lists some SO_2 oxidation data generated in a laboratory flow-through reactor. However, even though effective in controlling sulfates, the addition of Rh to Pt catalysts results in a significant increase in the filter regeneration temperature.

Table 2-17. Catalytic Oxidation Of SO_2*.

Pt:Rh Ratio (wt.)	SO_2 Conversion, %
100% Pt	41
10 Pt : 1 Rh	33
5 Pt : 1 Rh	13
3 Pt : 1 Rh	6
1 Pt : 1 Rh	7

* - Catalyst loading 1.77 g/dm^3 (50 g/ft^3), catalyst volume 0.9 dm^3, gas flow 1.7 Nm^3/h, 300 ppm SO_2, temperature 400°C

Theoretically, the sulfate make in active noble metal filter catalysts can be controlled using a number of methods that were developed for selective diesel oxidation catalysts, e.g., through the use of low Pt loadings or sulfate-suppressing additives. However, as it was the case in the above Pt/Rh catalyst example, one always has to accept a penalty in the catalytic activity when designing a more selective catalyst. In particulate filters, such penalty manifests itself as deterioration in filter regeneration performance. In other words, sulfate-suppressed CDPFs require higher exhaust temperatures for problem-free operation. Since in most CDPF applications no regeneration penalty can be accepted, the preferred method of sulfate control in catalyzed filters is through the use of ultra low sulfur fuel.

Base Metal Catalysts: Vanadium is one of the most popular base metal catalysts used for diesel particulate filters. The CDPF commercialized in Mercedes cars in California in the mid-1980's, mentioned earlier, was coated with a vanadium pentoxide (V_2O_5) catalyst by Degussa. This catalyst provided filter regeneration at temperatures of 380-400°C.

One of the potential problems with vanadium based catalysts is the volatility of V_2O_5 at higher temperatures, as may be encountered during filter regeneration. The evaporation of V_2O_5 may lead to gradual catalyst losses and shorten the filter lifespan, not to mention vanadium emission problems. Catalysts were developed that utilized vanadium compounds other than V_2O_5, for example silver or copper vanadates. An example copper vanadate base metal catalyst was developed by Heraeus.[157] The catalyst was prepared by doping and calcining copper vanadate $Cu_3V_2O_8$ with potassium carbonate in the molar ratio Cu:V:K 3:2:0.13. Diesel filters were then coated with the catalyst from a water suspension. The catalyst loading was between 10 and 80 g per 1 m^2 of the filtration surface area. Soot ignition temperature measured by the differential thermal analysis amounted to 365°C with this catalyst and to 500°C without catalyst.

C.6.2.4. Emission Performance

PM Filtration Efficiency: As with any type of diesel filter, the filtration efficiency for solid fractions of diesel particulates, including inorganic carbon and metal ashes, is determined by the properties of the filter substrate. Most catalyzed particulate filters use wall-flow monoliths of proven, high efficiency in capturing of solid particulates. The filtration efficiency increases with increasing soot load in the filter. Somewhat lower efficiencies are seen when soot is collected within the pore network in the walls during the initial filtration period. After a layer of soot stabilizes in the monolith channels, the efficiency for solid particulates increase to typically between 95 percent and nearly 100 percent.

The large differences in reported total filtration efficiency of catalyzed filters, which usually varies between some 60 and 95 percent, can be explained by the filter activity towards non-solid fractions of diesel particulates - sulfate particulates and the organic fraction of PM, known as SOF. As discussed earlier, most of these compounds are passing through the filter as vapors, especially at higher exhaust temperatures. Being a part of the gas phase, these compounds cannot be trapped and retained in the filter the way solid particulates are. Rather, their transformation in the CDPF depends entirely on chemical reactions that may occur upon contact with the filter catalyst.

At high exhaust temperatures, CDPFs may generate sulfates by catalytic oxidation of the exhaust SO_2 to SO_3, the precursor of sulfuric acid. At high temperatures, the gaseous SO_3 can penetrate the porous walls and freely leave the filter. Later, it combines with water and forms sulfate particulates when cooled down in the PM sampling system. The "sulfate make" may be a big problem with catalyzed filters. When fuels of higher sulfur content are used on clean diesel engines, catalyzed traps may even increase the total particulate matter output, i.e. exhibit an overall negative filtration efficiency. This will happen when the quantity of generated sulfates is higher than the amount of particulates trapped in the filer.

Platinum has the strongest tendency to form sulfates among all diesel filter catalysts. Most sulfates are typically formed over platinum catalysts at relatively high exhaust temperatures of about 350-450°C. Active, high Pt loading catalysts can effectively control total PM emissions only in conjunction with ultra low sulfur fuels, which contain insufficient amount of sulfur to cause problems, even if most of it would be oxidized to sulfates. Active catalysts can convert as much as 50 percent and more of the exhaust SO_2 to sulfates. Fuels of 300-500 ppm by weight sulfur, commonly referred to as "low sulfur fuels", can still cause considerable sulfate emission problems.

PM conversion efficiency in a noble metal catalyzed filter at different levels of sulfur in the fuel is shown in Figure 2-75.[105] Particulate emissions were measured over three engine test procedures, as indicated in the graph, all of which were characterized by high temperatures which favored the sulfate make. PM reduction efficiencies between 93-95 percent were measured with 3 ppm sulfur fuel. When 30 ppm sulfur fuel was used, the efficiency dropped to 72-80 percent. The CDPF efficiency decreased to zero at about 150 ppm sulfur content (with some differences between the test cycles). At that point, the amount of sulfate generated in the CDPF became approximately equal to the amount of solid particulates captured in the filter. The efficiency of the CDPF with the US ultra low sulfur fuel of 15 ppm sulfur interpolated over the ESC test would be 88 percent.
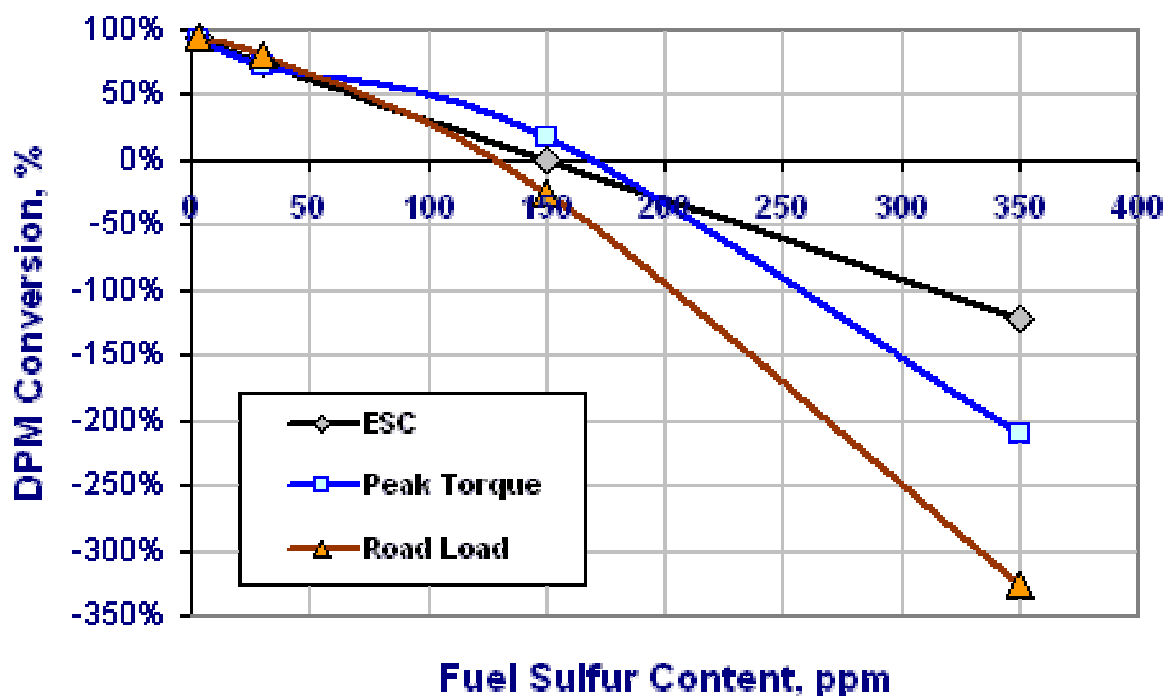
Figure 2-75. Conversion of diesel particulate matter (DPM) in PT-based CDPF at different fuel sulfur levels. *(CDPF: 10.5" dia. × 12", 100 cpsi, 17 mil wall; Engine: CAT 3126, 6 cyl., 7.2 liter, 205 kW (275 hp) @2200 rpm).*

It should be emphasized that the sulfate considerations depend on the regulatory definition of diesel particulate matter. It is common in occupational health regulations to exclude sulfates from PM definition and measure PM as either total carbon (i.e., inorganic carbon + SOF; example: US non-coal mining[156] or elemental carbon (example: German occupational regulations).[157] If sulfates are neglected, catalyzed filters will show excellent filtration efficiencies, even with extremely high levels of sulfur in the fuel. Care must be taken, however, that active catalysts do not cause air quality problems with other pollutants, such as SO_3 or NO_2.

The soluable organic fraction (SOF) is also vaporized in the filter during high temperature operation and cannot be physically trapped. The SOF performance of the CDPF will depend on the activity and the temperature of the catalyst. An active catalyst, such as Pt, will oxidize the SOF vapors. However, if a low activity catalyst is used, such as some base metal catalysts, the SOF vapors may pass through the filter. As a result, the CDPF may show decreased DPM filtration efficiency.

CDPF are also very effective in reducing particle (and nanoparticle) number emissions, provided the nanoparticles are solid. If liquid nanoparticles, such as composed of sulfuric acid or hydrocarbons, are created through condensation downstream of the filter, they obviously cannot be controlled by the CDPF. The formation of nanoparticles after the CDPF increases with the fuel sulfur content and with temperature. In a study with fuel of 371 ppm sulfur fuel a CDPF was found to decrease particle numbers by about 80 percent at a low temperature mode, and increase particulate numbers by some 140 percent (due to an estimated over 300 percent increase in sulfates) at a high temperature mode.

Gaseous Emissions Performance: Catalyzed particulate filters also facilitate a numbers of oxidation reactions in the gas phase, which are similar to those occurring in the diesel oxidation catalyst. Gaseous emission performance of a CDPF varies depending on the type and activity of catalyst. In general, platinum based catalysts, especially those with high Pt loadings, will be very active in the oxidation of hydrocarbons and carbon monoxide. On the other hand, some base metal catalysts used in diesel filters are quite inactive in respect to the gas phase components. They do not cause significant changes in the concentrations of CO and HC.

Platinum based CDPFs typically achieve about 80-90 percent conversion of CO. The example data in Figure 2-76[158] showing 95 percent CO conversion was generated on the ESC test cycle, characterized by high average load factors and high exhaust temperatures which favor catalytic reactions. It should be mentioned that the carbon monoxide performance also depends on the regeneration cycle. If a filter overloaded with particulates rapidly regenerates, there might be temporary shortage of oxygen leading to partial combustion of soot. Under such conditions secondary CO emissions can be generated in the filter. We are not familiar with any literature data showing how these temporary conditions may affect the total CO emission reduction over the vehicle duty cycle.
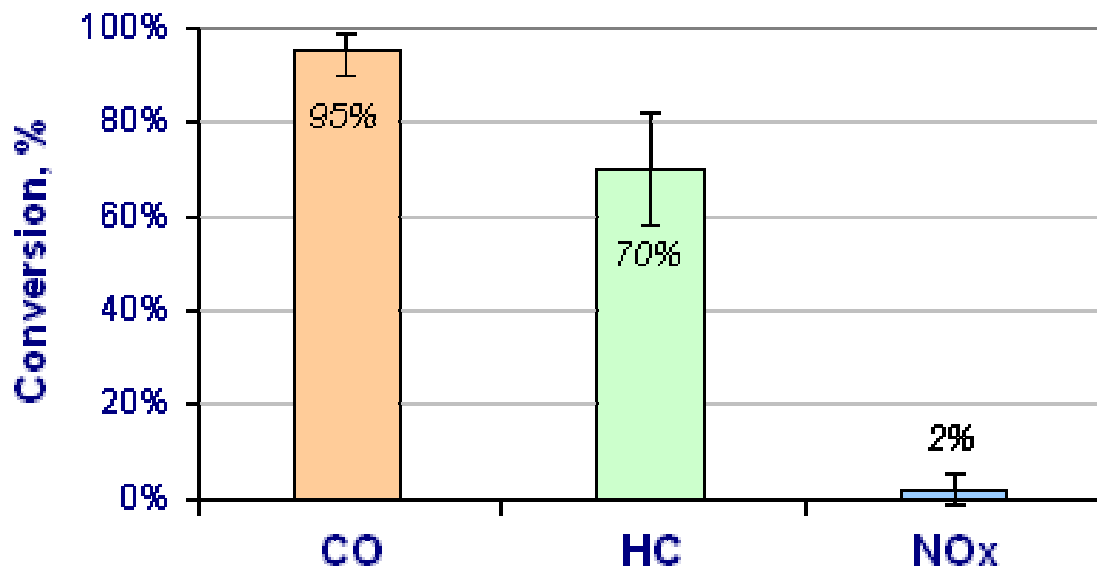
Figure 2-76. Conversion of gases in Pt-based CDPF.
[ESC (OICA) test cycle; CDPF and engine as in Figure 2-75; Data shown represents averages from several measurements with fuel sulfur changing from 3 ... 350 ppm].

Pt CDPFs typically show a 60-70 percent conversion of hydrocarbons due to catalytic oxidation, as shown in Figure 2-76[158] and confirmed by other studies.[159] A slight reduction of NO_x emission, which is typically measured in CDPFs (between 4.9 percent and -1.5 percent in Figure 2-76), is likely caused by internal exhaust gas recirculation due to increased pressure levels in the exhaust manifold, rather than by catalytic reactions. However, just like other oxidation catalysts, CDPFs also change the proportion between NO_x constituents (NO_2/NO) by increasing the NO_2 emissions through the oxidation of NO. Although there is no change in the total NO_x emission, that phenomenon is perceived as a disadvantage, due to the

high toxicity of nitrogen dioxide (occupational health!) and possible effects on ozone formation. Example data from chassis dynamometer tests of CDPF-equipped school buses is shown in Figure 2-77.[160] The particulate filter increased NO_2 levels from below 5 percent to about 30 percent of the total NO_x. This increase is generally comparable to that measured in the CRT filter, which produced NO_2 levels ranging from 26 to 34 percent when tested using the same test cycle and fuels (but different vehicles).[160] It can be speculated that filters with Pt catalysts at high loadings cause significant increase in NO_2, while some base metal formulations may be relatively inactive. The results in Figure 2-77 were obtained using platinum-containing CDPFs of undisclosed Pt loadings.
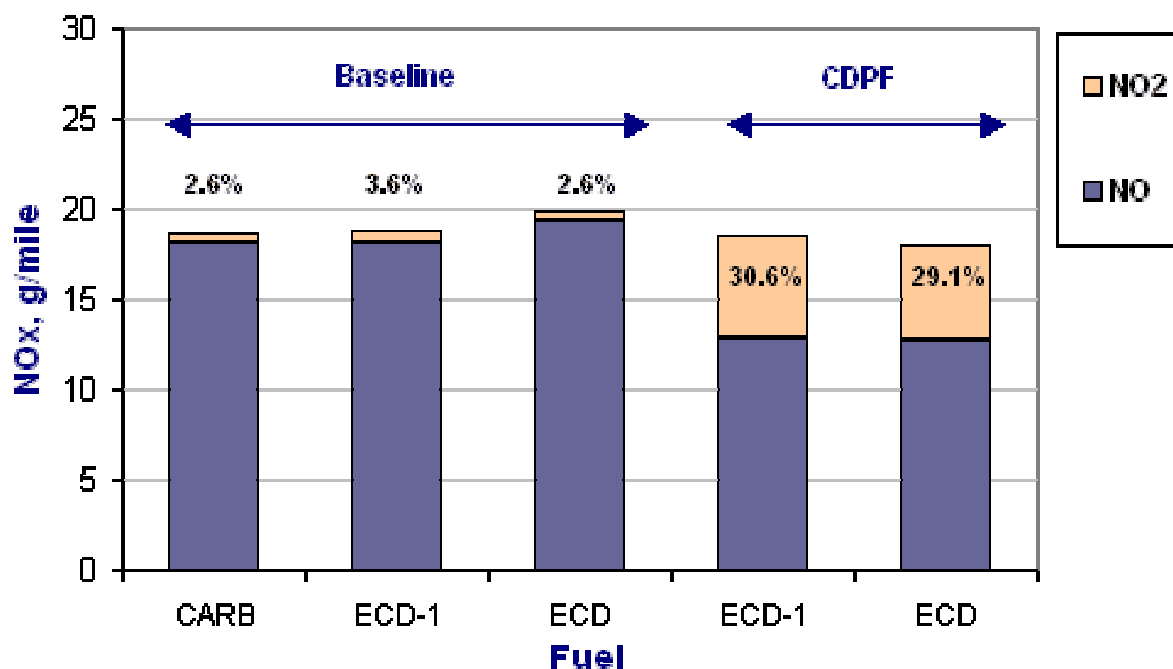
Figure 2- 77. Impact of CDPF on NO_2 emissions.
[Dynamometer driving cycle, average results from 2 school buses, CARB and ARCO (BP) EC diesel fuels].

Experiments with fuel sulfur levels changing from 3 to 350 ppm concluded that fuel sulfur does not significantly affect the CO, HC, and total NO_x performance of a platinum based CDPF.[158] Catalytic conversion of hydrocarbons also results in conversions of particulate SOF and other hydrocarbon derivatives, such as aldehydes or particle- and vapor-phase PAH. The conversion of aldehydes is typically higher than that of HCs and may exceed 90 percent. Conversions of PAHs after a CDPF were measured anywhere from less than 40 percent to as much as 97 percent, depending on the PAH type, association (particle or vapor phase) and test mode.[159] The filter used in the study had a relatively low Pt loading of 5 g/ft^3; CDPFs of higher Pt loadings would likely produce higher PAH conversions. Many PAHs were measured at levels below the minimum detectable limit of the measuring equipment, making it difficult to precisely quantify the effect of the CDPF. The same study found an increase of 1-nitropyrene after the CDPF at one engine mode. This nitro-PAH species could have been produced in catalytic reactions in the particulate filter, but could be also an artifact generated by reactions taking place in the PM sampling filter. The impact of the CDPF on the

mutagenic activity results, as determined by the Ames test, was inconclusive.[159] However, the samples in general showed very little mutagenic activity.

C.6.2.5. Regeneration and Pressure Drop

Catalyzed filters in their pure, passive form rely on the exhaust gas temperature for thermal regeneration. The temperatures required for soot oxidation, normally in the 500-600°C range, are lowered through the use of the catalyst to levels that are seen in real life operation of the engine, typically in the 320-420°C range. The exact mechanisms of the catalytic regeneration are not entirely understood. Heterogeneous catalytic processes in the gas phase occur on contact of gas molecules with the solid catalyst, i.e. the reactions take place on the surface of the solid phase. It is doubtful, however, that solid particulates, several orders of magnitude larger and heavier than gas molecules, have sufficient mobility to physically contact the catalyst. Furthermore, it would be only those particles that are deposited within the catalyzed pore network inside the walls or directly on the wall surface that would have such a chance. Obviously, particles that form layers inside the channel walls can never come in contact with the catalyst. A number of mechanisms are likely involved in the regeneration of catalyzed filters, as follows:

Catalytic oxidation by oxygen — particles are oxidized by oxygen atoms adsorbed on catalytic sites. This mechanism is limited to particles that physically contact catalytic sites. Oxidation of particle layers in the inlet channels would require that soot deposits are moved inside the filter by the impact of gas flow, as particles already in contact with the catalyst are oxidized to gaseous products.

Oxidation by nitrogen dioxide — NO_2, which is generated through catalytic oxidation of NO in the filter, can oxidize diesel soot at much lower temperatures than oxygen.[156] In a CDPF, this mechanism would apply primarily to particles positioned very close to or downstream of catalyst sites, generally within the pore network. Oxidation of the soot layer in the inlet channels, upstream of the catalyst would have to rely on a diffusional transfer of NO_2 countercurrently to the gas flow - not a very effective reactor design. This NO_2 effect, which is utilized to its full potential in the CRT Filter, is blocked by sulfur and requires the use of ultra low sulfur fuel.

Thermal oxidation by oxygen — catalytic oxidation of hydrocarbons and other gas species, as well as the carbon particulates themselves, can create local zones of increased temperature due to the exothermal heat of reaction. The increased temperature may be sufficient (> 500-600°C) to support non-catalytic, thermal oxidation of soot deposits. This oxidation mode is certainly important during uncontrolled regeneration, when temperatures increase well above 1000°C; its significance during continuous regeneration is not known.

As it is the case with catalytic processes, exhaust gas temperature is the most important factor influencing the filter regeneration. The rate of soot oxidation increases with the filter temperature. If the temperature is too low, soot accumulates in the filter causing excessive flow restriction, high exhaust gas pressure losses and, eventually, clogging of the unit. Units overloaded with soot are also prone to uncontrolled regenerations, which may be caused by a sudden "ignition" of the soot load accumulated in the CDPF, leading to a mechanical failure of the filter substrate (melting, cracking) due to excessive temperature or temperature stress.

In general, the minimum exhaust temperature required to sustain adequate self-regeneration of CDPFs varies between about 320-420°C. In practice, the temperature requirement it typically defined as the filter inlet temperature that must be reached over a certain minimum percentage of the engine operating time. Using an arbitrary example, one could require that, for a given CDPF application, a temperature of 350°C be reached or exceeded over at least 30 percent of the duty cycle. Commercial CDPFs offered for a number of nonroad applications over the 1990's typically required exhaust temperatures of 380-420°C over some 25 percent of the time. Lower exhaust temperatures are sufficient for filters used on newer, cleaner engines, especially in conjunction with ultra low sulfur fuel. One of commercial retrofit systems, the DPX filter by Engelhard, requires an *average* exhaust gas temperature of at least 225°C for use with a maximum 15 ppm sulfur fuel on post-1994 highway engines in California. Even though an average temperature specification cannot be directly compared with the previously given numbers, this application does represent a lower temperature requirement. Indeed, DPX filters of high Pt loading were demonstrated to operate on hybrid diesel-electric urban buses on duty cycles where exhaust temperatures hardly exceeded 300°C (winter months in New York City).[161] It should be remembered that the hybrid bus application is characterized by especially low engine-out PM emission due to the absence of rapid engine accelerations and other transients in the hybrid powertrain. Balance temperatures of the Engelhard filter, as measured in a laboratory as a function of the fuel sulfur content using a nonroad engine of higher PM emissions, are shown in Figure 2-78.[162] The balance temperature was determined using the DECSE 5-mode balance point test.
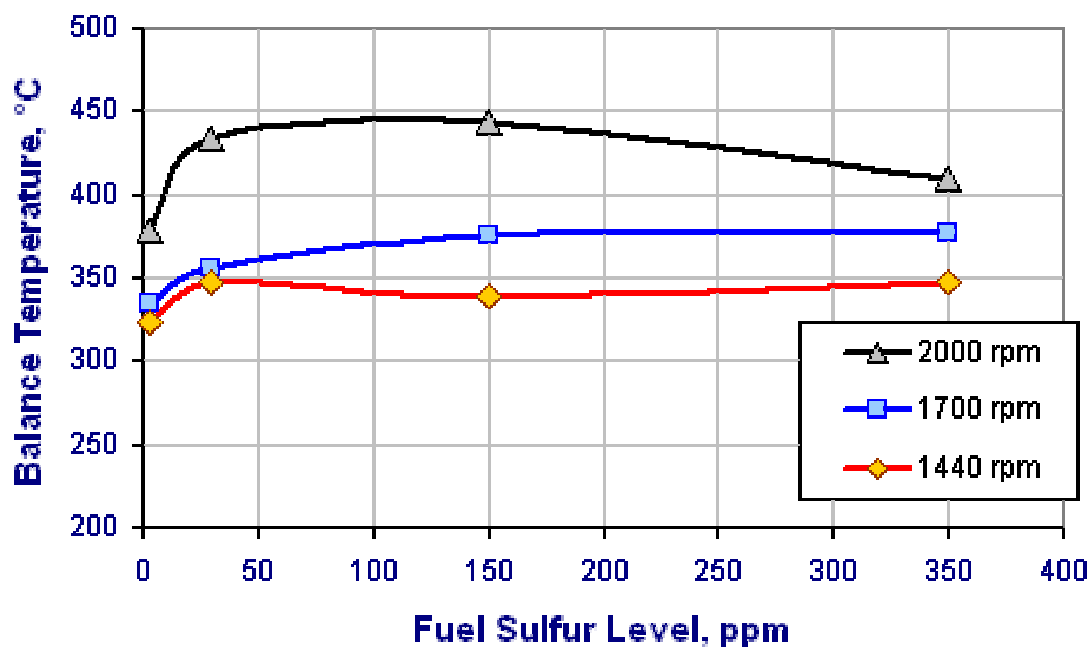
Figure 2-78. CDPF balance temperature at different fuel sulfur levels.

Laboratory determined balance temperatures, even though not necessarily a good approximation of the temperature requirements in the field, are very valuable in studying the relative changes of the balance point in response to changing system variables. Figure 2-78 illustrates such changes in response to changing fuel sulfur content and engine speed (exhaust

gas flow). There are more variables influencing the CDPF requirements in regards to the minimum operation temperatures. The most important factors can be summarized as follows:

Engine-out PM emission — CDPFs can regenerate at lower temperatures on cleaner engines. This finding is consistent with the theory of diesel filter regeneration.

Sulfur content in the fuel — decreasing the sulfur level from 30 to 3 ppm provided about 30°C improvement in the balance temperature (Figure 2-78). However, the balance temperature remained relatively constant when sulfur levels were further increased beyond 30 ppm.

Exhaust gas space velocity — increasing the engine speed and, as a consequence, the exhaust gas flow was found to increase the balance temperature (Figure 2-78). This finding would suggest that larger filters can regenerate at lower temperatures. However, increasing the filter size beyond a certain point is likely to deteriorate the regeneration due to the "extinguishing" effect of the filter heat capacity on transient temperature spikes.

In a suitable, high temperature application the regeneration of catalytic soot filters is practically continuous and loading and regeneration phases are not well pronounced. Rather, the unit is operating close to balance conditions and the amount of PM oxidized in the trap is approximately equal to the amount entering the trap. This kind of application is illustrated in Figure 2-79.[163] Exhaust gas pressure drop and temperature in the catalytic filter were recorded during more than 40 hours of operation on an underground mining vehicle. The engine, CAT 3306 PCTA rated 175 kW at 2200 rpm, was equipped with a ceramic monolith filter 15" diameter × 15", catalyzed with a base metal catalyst. Temperatures during periods with high engine load were constantly above 450°C. The corresponding pressure drop was fluctuating around 5 kPa (20" H_2O) with no apparent tendency to increase or decrease.
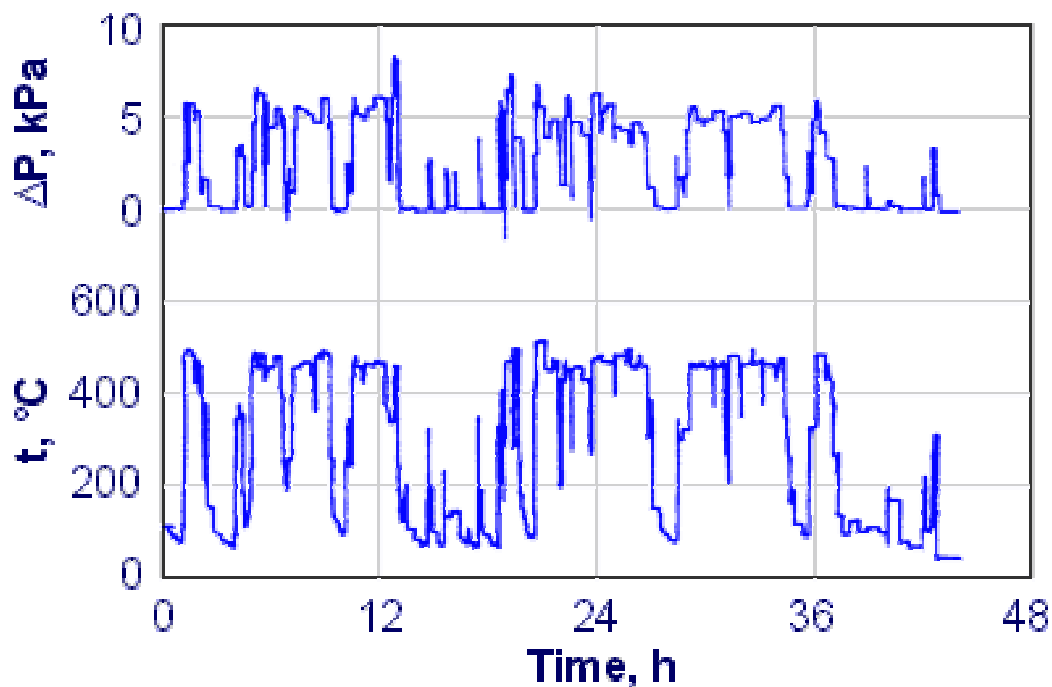
Figure 2-79. Pressure drop and temperature in a CDPF - high temperature application.

Applications with lower exhaust temperatures may experience a different regeneration and pressure drop pattern. Soot may accumulate during low temperature periods and then rapidly regenerate when the temperature increases, resulting in periodic regenerations. This type of CDPF operation is illustrated in Figure 2-80, which shows maximum engine backpressure data collected from six CDPF-equipped hybrid diesel electric urban buses during the New York City study.[161] The fluctuations of CDPF pressure drop are a clear indication that regeneration occurred periodically in all filter units. Such periodic regeneration pattern carries a danger of an uncontrolled regeneration, which occurs when excess soot becomes ignited during momentary high load operation. If engine speed drops to idle after the soot ignites, the exhaust flow becomes too low to carry away the heat released in the reaction. As a result, internal filter temperatures and/or temperature gradients become high enough to damage the filter substrate (the typical failure mode is melting for cordierite and cracking for SiC filters).

Among the six filters shown in Figure 2-80, three failed due to uncontrolled regeneration. All of the failed units were filters of low precious metal (platinum) loading, as indicated in the graph. However, even one of the high Pt loading units, which all survived the 6-month field test, had to be removed from the vehicle for cleaning to lower its excessive pressure drop.
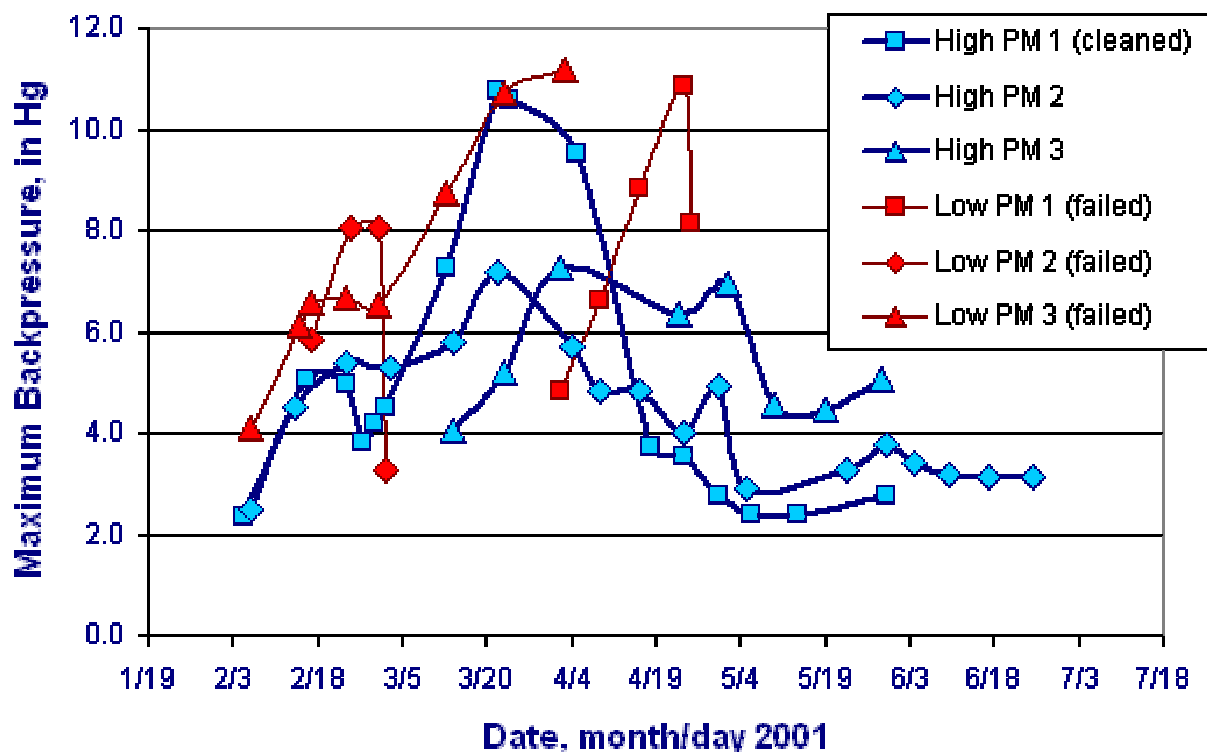
Figure 2-80. Pressure drop in a CDPF - low temperature application.

Exhaust gas temperatures were very low during the NYC hybrid study. In the winter months (February - March), the exhaust temperatures on most buses exceeded 300°C over only about 10 percent of the engine running time. During the following warmer months, the 10 percent temperature oscillated around 325°C. Filter regeneration was observed only once in several bus runs during cold weather conditions.

High pressure drop is one of the inherent features of all passive filters, including catalyzed diesel filters. Pressure drop on properly regenerating units in high temperature applications typically exceeds 5 kPa (20" H_2O). Low temperature applications experience higher exhaust gas pressure losses. Maximum engine backpressure levels exceeding 6" Hg (20 kPa = 80" H_2O) and more are not uncommon in Figure 2-80. Pressure loss levels of similar magnitude are reported in a number of other field test reports. The filter pressure drop is causing a certain fuel economy penalty associated with this technology which is usually estimated between 2 and 4 percent. A fuel economy penalty up to 2 percent was associated with particulate filters by the DECSE program, which carried out its measurements on a test bench, with filters properly regenerating on relatively hot test cycles. An average fuel economy penalty measured for the CDPF device on the ESC (OICA) cycle amounted to 0.5 percent.

C.6.2.6. Durability

Long term durability is the most important issue with catalyzed particulate filters, especially in the fully passive configuration. Since filter regeneration depends on the duty cycle, it is very difficult, if not impossible, to ensure failure free operation under all possible operating conditions and duty cycles. Even on hot engines, a single period of extended idling can lead to overloading of the filter with soot, followed by an uncontrolled regeneration and catastrophic failure.

Proper engine maintenance is also of critical importance in assuring long filter life. In particular, filter catalysts are typically sensitive to poisoning by lubricating oil and its additives. CDPF equipped engines must be well maintained to avoid excessive oil consumption. Engine failures resulting in oil leaks to the exhaust system may result in immediate deactivation of the catalyzed filter.

In OEM applications CDPFs will most likely require some kind of active regeneration support in cases excessive soot load (pressure drop) is detected in the filter. Such measures may involve, for example, increasing the exhaust gas temperature through special engine management strategies. In retrofit applications, long filter lifespan can be ensured through (1) careful verification (recording) of the exhaust temperature during real operation of the vehicle prior to retrofitting, (2) providing high level of engine maintenance (oil consumption!) after the retrofit, and (3) monitoring the exhaust backpressure on the retrofitted vehicle for early detection of problems. Filter pressure drop monitors, which can be connected to dashboard-installed warning lights and/or the engine control module, are available with most commercial CDPF systems. The use of such monitors with CDPFs is actually required in some retrofit programs.[164] Excessively high pressure drop is an indication that the filter accumulated too much soot and may be facing an uncontrolled regeneration or plugging. In either case, the unit must be taken off the vehicle and cleaned. Low pressure drop levels, on the other hand, may be an indication that the filter has already lost its mechanical integrity and is leaking unfiltered exhaust gas. It must be realized that proper implementation of such CDPF monitoring program may result in noticeable increase in the amount and cost of the engine and vehicle maintenance.

Experience from underground mining indicates that the lifetime of a CDPF installed on a suitable, high temperature application varies between 5,000 and 10,000 engine hours. However, the average filter life is shorter due to premature filter failures in unsuitable

applications (cold engine duty cycle, engine maintenance problems, etc.). According to US Bureau of Mines estimates from the early 1990's, the average CDPF durability in underground mines was about 2,500 hours.

Durability of filters in OEM applications has to meet the regulatory emission durability requirements. The first CDPF-equipped engine that was emission certified in the US - MY2001 Navistar 530 for school bus application - has been classified as a medium-heavy-duty engine of a 185,000 miles required emission durability. In the certification process, the manufacturer demonstrated this durability through accelerated 1000-hour engine dynamometer aging of the CDPF. Particulate filter manufacturers who verified CDPF systems for the California diesel retrofit program, announced in 2000, had to demonstrate emission durability of 150,000 miles and provide product warranty for 100,000 miles. At this time there is insufficient data to estimate the average CDPF life and failure rates in real field operation.

Another source of increased maintenance in CDPF-equipped engines is related to ash emissions. Just like other types of filter systems, CDPFs retain most of metal oxide ash emissions that are generated (primarily) from lube oil additives. Since ashes are incombustible, their accumulation causes steady increase in the filter pressure drop. This problem may be partially alleviated by periodic cleaning of the filter using compressed air, steam, water, or other means (cleaning operations should conform to the manufacturers' recommendations to avoid any detrimental effect to the catalyst). Early experience from retrofit installations in the UK in the late 1990's indicates that de-ashing of CDPFs may be needed as often as every 30,000 km. On the other hand, some field studies of CDPF retrofits in the U.S. found that maintenance/de-ashing intervals may be as long as 240,000 km (150,000 miles), exceeding the CDPF manufacturer recommendation of 60,000 miles.[160] These huge differences are likely caused by different engine technologies and lubricating oil quality, but more experience is needed to draw any conclusions. Filter cleaning intervals can be certainly maximized through the use of low ash lube oils.

C.6.3. Continuously-Regenerated Trap (CRT)

The CRT ("Continuously Regenerating Technology"; originally introduced as "Continuously Regenerating Trap") is a trade name for a catalytic, two-stage, passive particulate filter system capable of regenerating at temperatures of below 300°C on a suitable application and with the use of ultra low sulfur diesel fuel. The principle of CRT regeneration is based on the finding, discovered and patented by Johnson Matthey, that diesel particulate matter (PM) is more easily oxidized by nitrogen dioxide (NO_2) than by oxygen.[156] Carbon in the form of soot is oxidized by oxygen with noticeable reaction rates at temperatures above 550°C. With NO_2, the process occurs at temperatures as low as 250°C, as illustrated by the laboratory reactor data in Figure 2-81.[165]
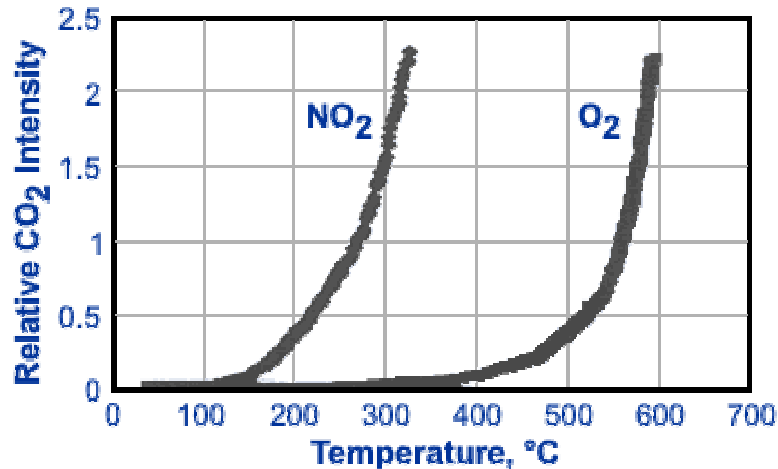
Figure 2-81. Oxidation of PM by oxygen and nitrogen dioxide.

A schematic of the CRT configuration is shown in Figure 2-82. The CRT is composed of two devices - an oxidation catalyst (upstream) and a ceramic wall-flow diesel filter (downstream). The NO_2 necessary for filter regeneration is generated in the oxidation catalyst from nitric oxide (NO) present in diesel exhaust, according to the following reaction:

$$NO + \tfrac{1}{2}O_2 \leftrightarrow NO_2 \qquad\qquad (1)$$

Diesel particulate matter (PM) which is being trapped in the filter is continuously oxidized by NO_2, as follows:

$$NO_2 + C \rightarrow NO + CO \qquad\qquad (2)$$

$$NO_2 + C \rightarrow \tfrac{1}{2}N_2 + CO_2 \qquad\qquad (3)$$

where C (carbon) represents the combustible portion of PM.

Theoretically, in the process of PM oxidation NO_2 may be reduced to both NO and N_2 as shown in Equation (2) and (3), respectively. In practice, most of the NO_2 reacts with carbon to re-create the nitric oxide, Equation (2). The oxidation of soot is further enhanced by the exhaust water vapor, presumably due to the formation of HNO_3 from NO_2 and H_2O, which also reacts with carbon. From the existing literature reports it is not clear if nitrous oxide, N_2O, is also present among the reaction products.
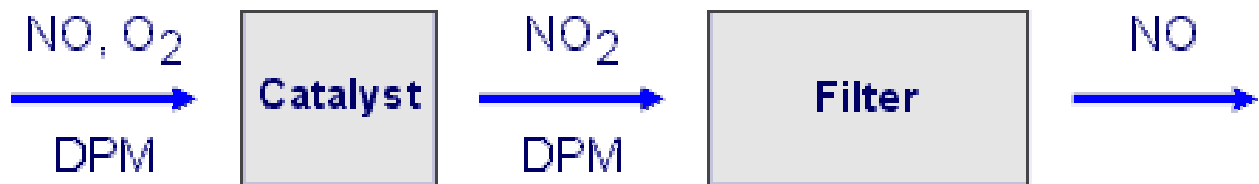
Figure 2-82. CRT filter: configuration and principle of operation.

C.6.3.1. Catalytic Oxidation of NO in CRT Filter

Engine-out NO_x emissions from diesel engines are typically composed in about 95 percent of NO and in 5 percent of NO_2. Depending on temperature, the catalyst part of the CRT can increase the NO_2 fraction to about 50 percent or more of total NO_x. The oxidation of NO to NO_2, as expressed by Equation (1), is an equilibrium process controlled by the reaction kinetics at lower temperatures, and by thermodynamic constrains at high temperatures, as illustrated in Figure 2-83.[131] Four equilibrium lines shown in the graph were computed for different oxygen concentrations. When operating at low temperatures, in the kinetically controlled regime, the conversion rate increases with the catalyst activity and temperature. Thus, NO conversion can be increased by using a more active catalyst or by increasing the catalyst size. At higher temperatures the NO/NO_2 shift is constrained thermodynamically. Increasing exhaust gas temperature in that region causes a decrease in NO conversion. The highest NO conversion occurs at medium temperatures of about 250-350°C, where, with the use of a sufficiently large and active catalyst, the NO_2 fraction can be increased to 70-80 percent of total NO_x.
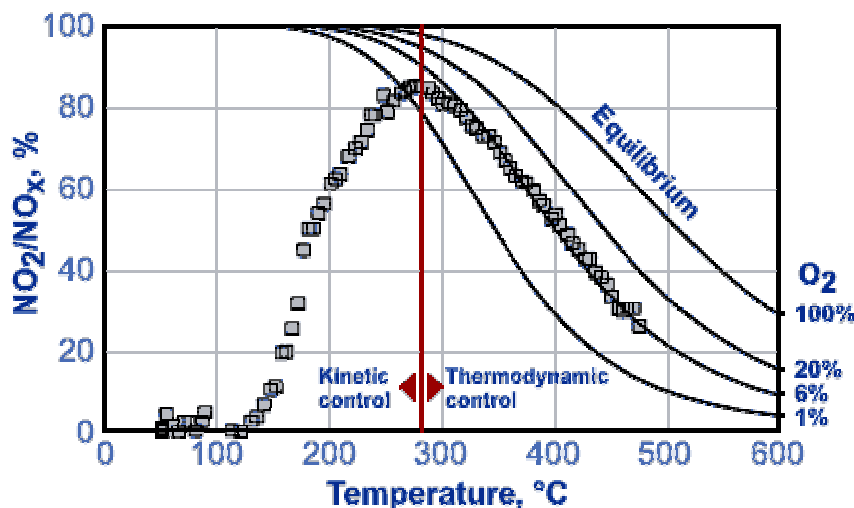
Figure 2-83. NO/NO_2 shift in oxidation catalyst.
(Catalyst: Pt, 50 g/ft^3; Gas: 270 ppm NO, 6% O_2, 10% H_2O in N_2).

Once the NO_2 enters the filter part of the CRT, it reacts with soot. The rate of this reaction (or the regeneration rate of the CRT) increases with temperature and with the NO_2 concentration. Thus, a certain excess in NO_2 is always needed to maintain appreciable reaction rates. The NO_2 levels at the CRT outlet are believed to be typically above 20 percent (but sometimes as high as 60 percent) of the total NO_x, which represents an increased level relative to the engine-out emission. Experiments show that the total NO_x emission is not changed over the CRT, indicating that most of NO_2 reverses to NO, according to Equation (2). The reaction to N_2 given by Equation (3) apparently plays little role in CRT regeneration.

The regeneration of the system can be enhanced, within certain limits, by increasing the size of the catalyst and the filter and/or by increasing the noble metal loading in the catalyst. Nevertheless, a successful passive operation of the CRT requires that the exhaust gas reaches a

sufficient temperature and meets certain conditions, as discussed below. As it is the case with regeneration of all passive filter systems, the CRT operation depends on the vehicle's duty cycle. If the application is unsuitable or the duty cycle is too cold, the filter may be plugged with soot or experience uncontrolled regenerations.

C.6.3.2. Comparison with Alternative Configurations

Passive catalytic filter systems can be configured as the CRT, the catalyzed diesel particulate filter (CDPF), or as a combination of both. These three configurations are schematically shown in Figure 2-84. The "classic" CRT involves a combination of an oxidation catalyst and an uncatalyzed filter. In the CDPF, the catalyst is coated directly onto the wall-flow monolith. The combined system includes an oxidation catalyst, followed by a CDPF.
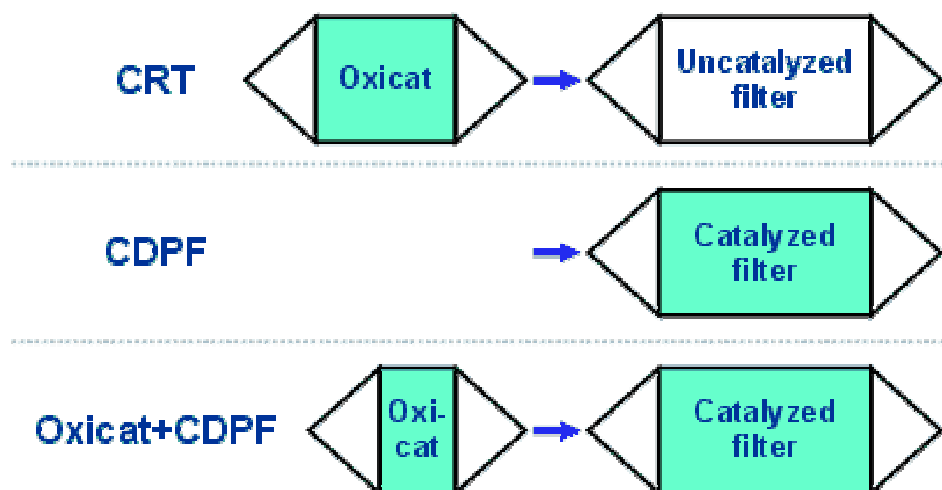
Figure 2-84. Configurations of catalytic filters.

As discussed above, the CRT depends exclusively and completely on the NO_2 effect for regeneration. The CDPF regeneration, on the other hand, occurs due to a number of mechanisms relying on both oxygen and NO_2 as the oxidants. In particular, the NO_2 regeneration mechanism would also occur, to some degree, in CDPFs coated with active noble metal catalysts, such as platinum. The platinum catalyst will inadvertently generate some NO_2 with a beneficial effect on the filter regeneration. The CRT, however, features a superior reactor configuration that maximizes the NO_2 effect. In the CRT, the NO_2 is generated upstream of the filter and, thus, fully available for the oxidation of soot. In the catalyzed filter, NO_2 is generated within the monolith walls and is not available for the oxidation of the upstream portion of soot that may be collected in the inlet monolith channels. As a result, when CRT filters are operated on suitable, sufficiently high NO_x engines, they show a regeneration temperature advantage over catalyzed filters.

On the other hand, an NO_2 molecule in the CRT reactor can be used only once for the oxidation of soot. Once it reacts with carbon to form NO, it cannot be oxidized again to nitrogen dioxide and used for oxidation of further carbon molecules. This is a drawback of the CRT configuration, which can be overcome by combining both devices together. In such

combination, denoted as "oxicat + CDPF", the gas entering the filter is enriched in NO_2, just as is the case in the CRT. However, as NO particles re-created during regeneration pass through the catalyzed filter pores, they can be oxidized back to NO_2 over the active Pt catalyst sites. This second generation NO_2 can oxidize further carbon particles, thus increasing the regeneration performance in comparison to the classic CRT system. Regeneration rates in this configuration may be also further increased due to catalytic oxidation of carbon by oxygen.

Indeed, laboratory tests of the combined oxicat + CDPF configuration confirmed improved regeneration performance, both in terms of lowered balance temperatures and increased regeneration rates.[166] Balance temperatures, as determined on an engine dynamometer test with a 3 ppm sulfur fuel, are listed in Table 2-18. The CRT shows a 15°C advantage over the CDPF. The combined oxicat + CDPF configuration yields an additional 10°C improvement in the balance temperature.

Table 2-18. Balance temperature comparison.

Configuration	Balance Temperature
CRT (oxicat + uncatalyzed DPF)	265°C
CDPF	280°C
Oxicat + CDPF	250°C

Increased regeneration rates in the oxicat + CDPF configuration, measured as the rate of pressure drop reduction over time in soot-preloaded filters, is shown in Figure 2-85. All three filters were preloaded to the same soot loading of about 6 g/liter (the CDPF pressure drop is slightly less than in the other configurations due to the absence of the upstream catalyst substrate). Clearly, the combined configuration shows a significant advantage over both the CDPF and the CRT. The Pt loadings in the filters were not disclosed, but the catalyst volume in the oxicat + CDPF configuration was half of that in the CRT, while the Pt loading per unit of catalyst volume was constant resulting in a decrease in the total amount of platinum in the combined system, relative to the CRT.
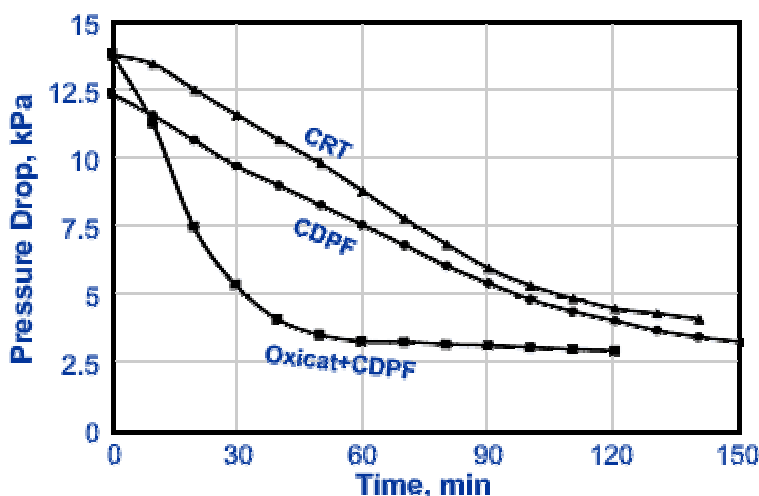
Figure 2-85. Comparison of regeneration rates in various catalytic filter configurations.

The above data indicates that the oxicat + CDPF system may very well be the best configuration for a passive, catalytic diesel particulate filter, which could combine the advantages of both the CRT and the CDPF at no cost increase in comparison to CRT. Johnson Matthey has been working on the optimization of the balance of catalytic activity between the pre-catalyst and the catalyzed filter. The system is expected to be commercialized under the trade name CCRT™ and offered in parallel with the CRT configuration.

C.6.3.3. Application Limits

Exhaust gas temperature, NO_x/PM ratio, and fuel sulfur content are the major factors that influence the CRT emission performance and regeneration. The following are the CRT application limits:

- Exhaust gas temperature — 275°C (minimum)

- Sulfur content in the fuel — 50 ppm wt. (maximum)

- Exhaust NO_x/PM ratio — between 8:1 - 25:1 (by weight, minimum)

The above numbers, based on the recommendations by the CRT manufacturer Johnson Matthey, should be considered simplified guidelines. They do not account for such important aspects of real-life operation as variability in engine-out PM emissions or fluctuations of parameters under transient conditions. There is also a certain trade-off between various parameters, such as the exhaust gas temperature requirement may be lowered by lowering the fuel sulfur content, increasing the NO_x/PM ratio, or operating the CRT on a cleaner (lower PM emission) engine.

To sustain fully passive operation (regeneration), the CRT filter requires a certain minimum level of *exhaust gas temperature*. CRT filter system verified by the California ARB for retrofitting post-1994 highway engines require exhaust temperatures exceeding 270°C over at least 40 percent of the operating time (fuel sulfur $\leq$ 15 ppm). Example CRT balance temperatures, determined on a CAT 3126 industrial engine using the DECSE method, for a range of fuel sulfur levels and engine speeds are shown in Figure 2-86.[158] As seen in the graph, the filter could regenerate at low temperatures of around 300°C, provided ultra low sulfur fuel was used. The engine used in this study had a relatively high PM baseline; it is possible that somewhat lower balance temperatures would be measured on a cleaner diesel engine.

As long as ultra low sulfur fuel is used, the CRT has a balance temperature advantage over the catalyzed filter. Relatively high average balance temperature advantage of 60°C was found by the DECSE study.[158] As shown before (Table 2-18), a much smaller advantage of 15 °C was reported by others.[166] Since balance temperatures depend on a number of engine specific parameters (e.g., NO_x/PM ratio), any generalization is difficult.
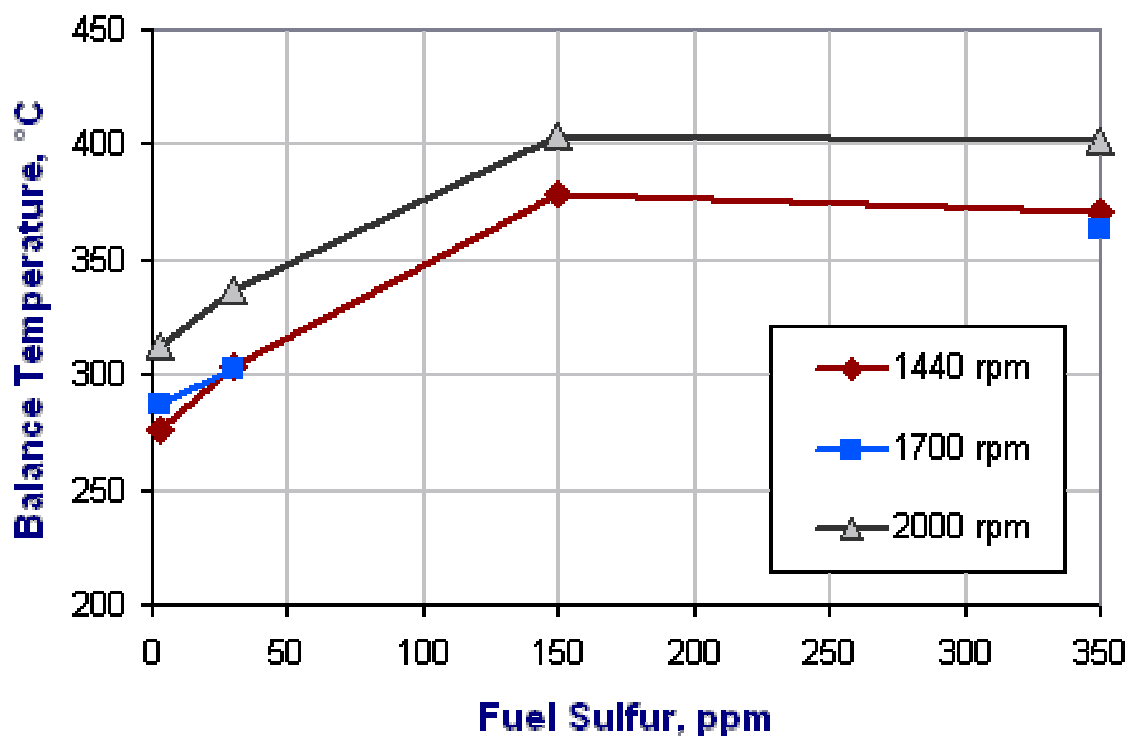
Figure 2-86. CRT balance temperature as a function of fuel sulfur level.

At higher *sulfur levels* the CRT regeneration deteriorates. It is believed that sulfur dioxide (SO_2) adsorbs in strong competition to NO on the catalytically active sites in the catalyst element of the CRT. This competitive adsorption is blocking the active sites and lowers the NO/NO_2 shift in the catalyst, Equation (1). Because insufficient amounts of NO_2 are generated, the trap requires higher exhaust temperatures to regenerate. This deactivation by sulfur has a temporary character. Filters deactivated by operation on high sulfur fuels regain their ability to regenerate when operated for a period of time on ultra low sulfur fuels.[158] Most of the experience with CRT systems has been accumulated using fuels of a maximum sulfur content of 10 ppm, such as the Swedish Environmental Class 1 diesel. Tests with higher sulfur levels indicate that fuels of up to 50 ppm sulfur may be still satisfactory.

Another reason for using ultra low sulfur fuels with the CRT system is catalytic oxidation of SO_2. To maximize the NO/NO_2 conversion, a very active oxidation catalyst formulation is used in the CRT. That catalyst is also effective in oxidizing SO_2 to SO_3 and, thus, in producing sulfate particulates. The nucleation of sulfate particulates occurs after gases leave the filter, leading to an observed decrease in the PM filtration efficiency. This effect depends on the fuel sulfur content and the exhaust temperature, as shown in Figure 2-87. Experiments with 500 ppm sulfur fuel showed that at temperatures above 400°C the filter was increasing the total particulate emission to double the engine PM baseline.[167]
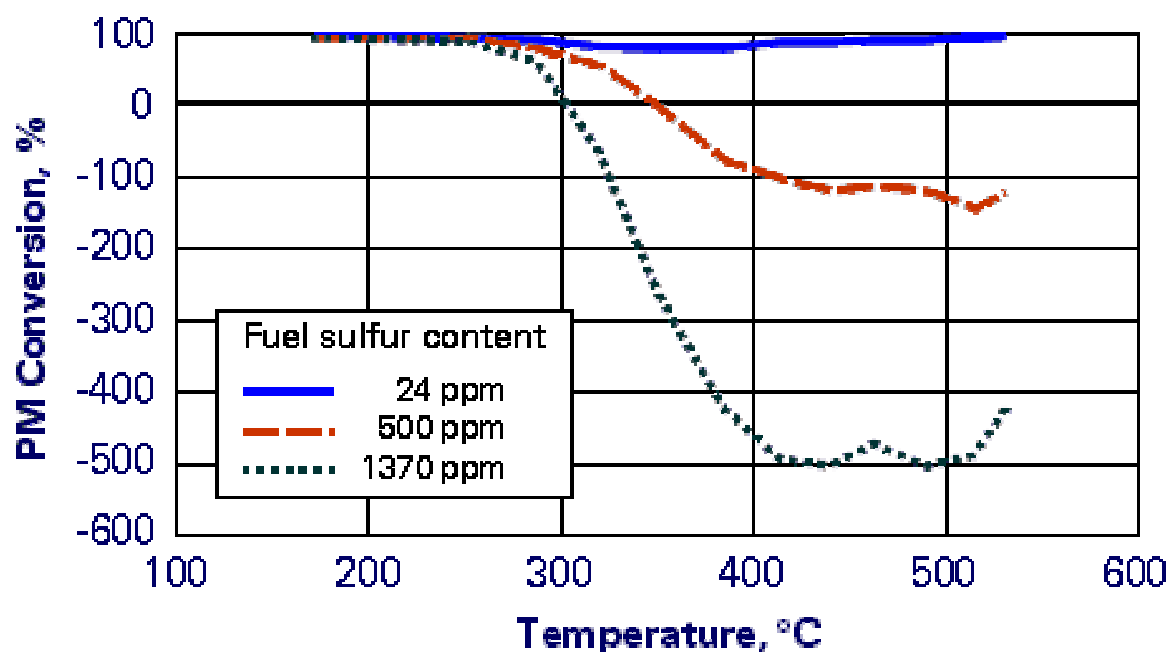
Figure 2-87. Effect of fuel sulfur content on PM conversion in the CRT.

An important limitation of the CRT regeneration is its dependence on the *NOx/PM ratio* in the engine-out emissions. The CRT configuration in its "classic" form uses an uncatalyzed filter and, thus, depends exclusively on NO_2 for regeneration. Higher NO_x/PM ratios result in higher NO_2 concentrations and better filter regeneration.

The theoretical minimum NO_x/PM ratio can be calculated based on the stoichiometry of reactions given by Equation (1) and (2). If all NO was converted to NO_2, which then would entirely revert to NO during regeneration, the required NO_x/PM ratio would be 3.83:1 (NO_x as NO_2 equivalent, PM as pure carbon). In practice, however, neither all of the engine-out NO can be converted to NO_2, nor the entire NO_2 that was generated can be used in the regeneration process. In several earlier publications, the minimum NO_x/PM ratio required by the CRT was typically listed at 8:1.[168] Minimum NO_x/PM ratios as high as 20:1 - 25:1 have been referenced as "sufficient in most applications" in newer literature.[169]

Again, there is some trade-off between the different parameters that influence CRT performance. For instance, installations with high NO_x/PM ratios may be able to regenerate at lower exhaust temperatures. On the other hand, low NO_x emission engines may not be the ideal candidates for CRT application.

C.6.3.4. Filter System Design

The system consists of two functional components packaged in one housing as shown in Figure 2-88. The first component is an active oxidation catalyst, the second component is a ceramic wall-flow diesel filter. For the oxidation catalyst usually a 400 cpsi ceramic substrate is normally used. Since the best activity for NO oxidation is achieved in the Pt/Al_2O_3 system, the catalyst is usually a high loading of platinum on alumina washcoat. The Pt loading in commercial products is not disclosed, but catalysts of 80 g/ft^3 Pt were considered during CRT

system development.[170] Current state-of-the-art is thought to be less than 50 g/ft^3 of Pt loading. The particulate filter in most applications has been a commercial, uncatalyzed cordierite wall-flow honeycomb of 100 cpsi and 17 mil wall thickness. Other filter materials, such as SiC monoliths or sintered metal, can be also used in the CRT configuration.

In systems used for retrofitting of heavy-duty Euro 0 - Euro 2 truck and bus engines, the volume of the catalyst approximately matched the engine displacement, with the filter having twice the volume of the catalyst. For example, systems with catalysts of 8.5 liter volume (267 mm diameter $\times$ 152 mm = 10.5 $\times$ 6 in) and filters of 17 liter volume (267 mm diameter $\times$ 305 mm = 10.5 $\times$ 12 in) were used for retrofitting of engines between 7 and 11 liters displacement.[167 The same size of CRT unit was used for testing on the CAT 3126, 7.2 liter, 205 kW @ 2200 rpm engine in the DECSE program.[162]
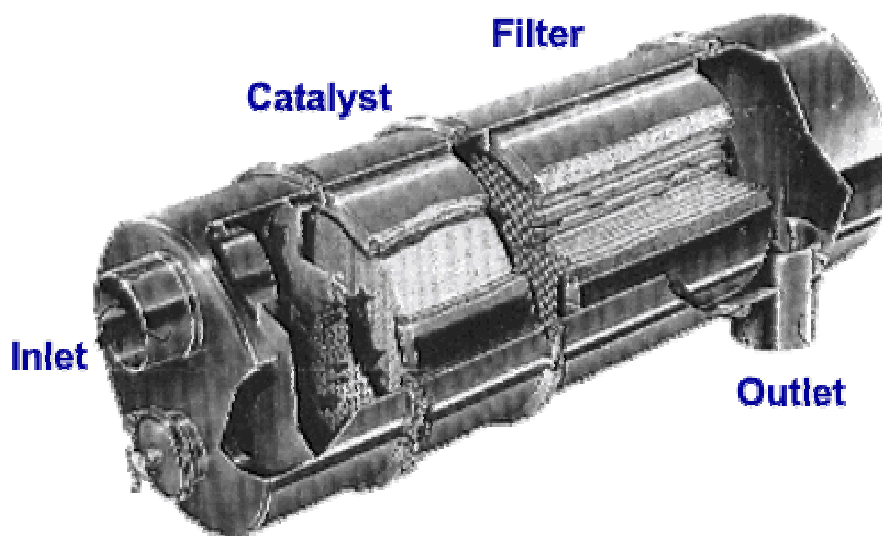
Figure 2-88. Cutaway view of CRT.

The CRT housing includes four stainless steel modules: inlet module, catalyst, filter and the outlet module. Modules are clamped together by three V-clamps. A bypass that opens in case of filter clogging may be provided in the inlet module.

The standard design uses the same diameter of oxidation catalyst and particulate filter. The system usually replaces the production silencer of the vehicle. The size of the system is similar to that of the silencer although the weight is higher. The modular design, shown in Figure 2-88, allows for simple replacements in case of a defect and minimizes the total number of different catalyst and filter models. The filter module can be axially turned to blow out the inorganic ash buildup and, thus, increase the filter life. An alternative design is a direct-fit replacement for the original muffler. In that case, the system is very easy to retrofit but the direction of flow through the filter cannot be changed.

C.6.3.5. Performance

Gases: The CRT, being a combination of catalyst and filter, influences the emissions of gaseous pollutants as well as the particulate matter. CO and HC emissions, based on test results from several heavy duty Euro 1 and Euro 2 engines, are reduced by about 85-95 percent when tested on the ECE R49, ESC, or ETC test cycles. Due to lower exhaust temperatures, the CO and HC performance is somewhat lower over the US FTP transient cycle, where conversions of about 70 – 90 percent were measured.[165]

Aldehydes, including formaldehyde and acetaldehyde, can be reduced by 50-90 percent and more. In a study on urban buses with 1999 DDC Series 50 engines, emission reductions greater then 90 percent were reported for CO and HC, over 99 percent reduction in carbonyls (aldehydes, ketones,…), up to 80 percent PAH reduction, and over 90 percent reduction in nitro-PAHs, all measured on CBD and NYB chassis dynamometer test cycles.[171]

Since most of the nitrogen dioxide consumed in regeneration reacts to NO rather than to nitrogen, there is no significant change in the total NO_x emissions over the CRT. The CRT system, like all systems incorporating active oxidation catalysts, changes the proportions between the nitrogen oxides, producing increased NO_2 emissions. NO_2 emissions may be disadvantageous in some situations, especially in occupational health environments such as underground mining. The NO_2 emission may also cause problems in other areas with poor air movement, e.g., in city streets of high rise buildings. NO_2/NO_x tailpipe ratios between 20 percent and 60 percent were measured with the CRT on different test cycles, as compared to about 5 percent in untreated diesel exhaust.[172] NO and NO_2 emissions measured from a CRT-equipped urban bus are illustrated in Figure 2-89.[173]
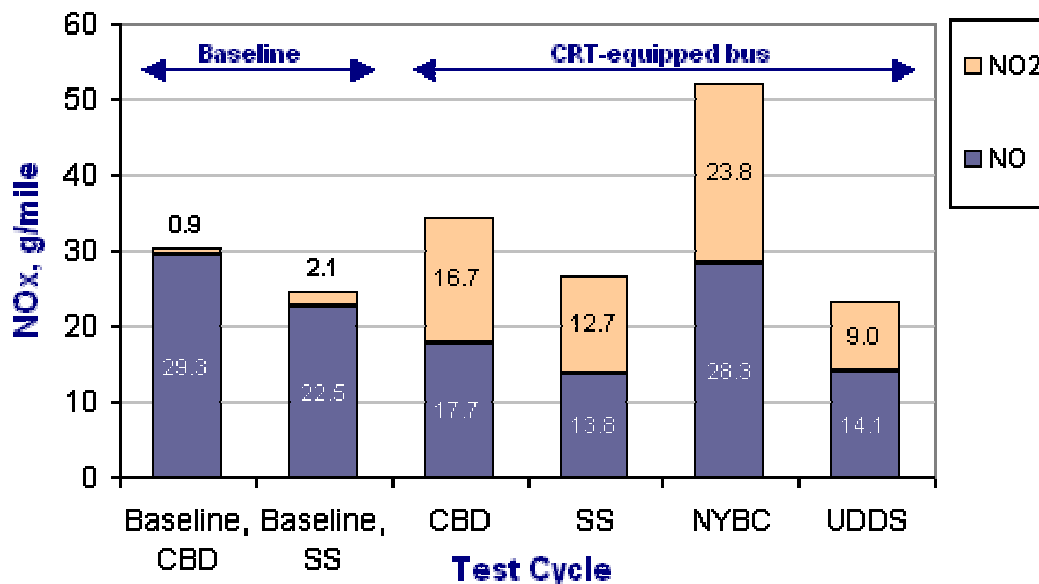
Figure 2-89. CRT effect on diesel bus NO_x emissions. *(1998 DDC Series 50 engine).*

Particulate Matter: The overall PM mass reduction efficiency depends on the conversion of the three fractions of diesel particulates: (1) solid carbon and ash, (2) SOF (heavy hydrocarbons), and (3) sulfate particulates. Since the CRT utilizes wall-flow monoliths of well proven, over 95 percent efficiency for solids, and an active oxidation catalyst which is fairly efficient in oxidizing SOF, the overall PM performance depends on sulfate particulates. The filtration efficiency decreases with increasing sulfur content in the fuel and with increasing exhaust gas temperature during the test cycle. Some results measured over the ESC (OICA) test cycle and at the peak torque condition are shown in Table 2-19.[162] The ESC cycle, due to its high average engine load and high exhaust temperature, may be considered disadvantageous for the CRT performance.

Table 2-19. PM reduction efficiency in CRT filter (CAT 3126 engine).

Fuel Sulfur Level, ppm	PM Reduction, %	
	ESC test	Peak Torque
3	95	91
30	72	73
150	-3	19
350	-155	-139

A number of studies using 10 - 30 ppm sulfur fuel reported total particulate matter reductions in the range of 90 percent. These reductions make it possible to meet Euro 4/5 PM emission standards using a CRT-equipped Euro 2 engine or to meet the US 2007 limits on a US 1994 engine. On today's light-duty diesel engines of about 0.2 g/mile PM emissions, the CRT can reduce PM to below 0.02 g/mile, which satisfies the requirements of both the Euro 4 and US Tier 2 regulations.[174]
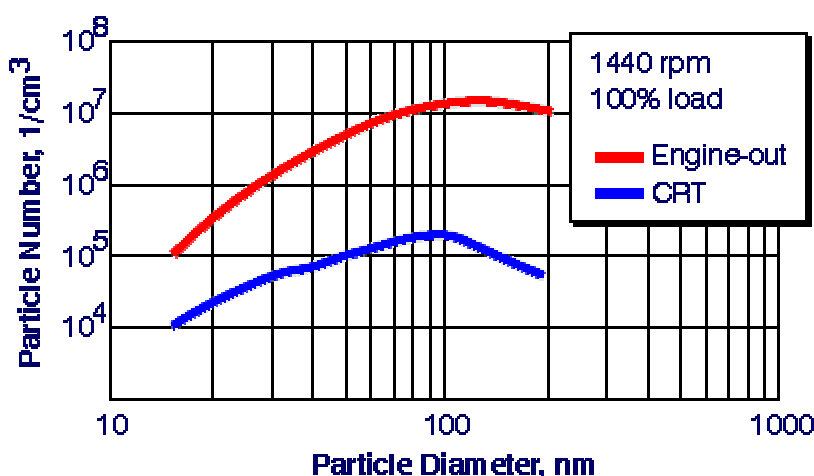
Figure 2-90. Particle size distribution with CRT trap.

The CRT trap was also reported to decrease the nanoparticle number emissions, Figure 2-90. The data was generated on a 6-cylinder, DI, turbocharged and intercooled Euro II diesel engine, rated 169 kW @ 2400 rpm.[175] Some filter systems increase the nanoparticle numbers, due to hydrocarbon and sulfate nucleation after the trap. It can be speculated that

little hydrocarbon material is available for such nucleation in the CRT, due to its high hydrocarbon and SOF removal efficiency.

C.6.3.6. Experience and Commercial Status

In countries that introduced ultra low sulfur diesel fuels, the CRT system is commercially available as an aftermarket kit from either Johnson Matthey or its licensed suppliers. Systems have been installed on buses and trucks mainly in Sweden but also in the UK, Germany, and other EU countries. Nearly all vehicles operate on Swedish Class 1 (10 ppm S) or equivalent fuel. Some systems are also tested on 50 ppm sulfur fuel. Few test run on sulfur-free biodiesel fuel. After 15 ppm sulfur diesel fuel became commercially available in California in 2000, the CRT system is also available in the US. About 19,000 vehicles have been equipped with CRT filters from the introduction of the system in 1994 through the year 2001 (18,000 in EU; 1,000 in the U.S.).[169]

CRT retrofits for heavy-duty engines regenerate as fully passive systems. As such, they require a careful selection of the engine and duty cycle to ensure sufficient exhaust gas temperatures, as well as NO_x/PM ratios, for problem free operation. In Europe, the manufacturer recommended that CRT systems be installed on turbocharged engines no older than MY 1985.

A durability study was conducted to determine the emission performance of in-use CRT systems.[165] Seven CRT systems that accumulated between 106,000 and 600,000 km in bus, truck, and train operation were evaluated. PM performance measurements, as determined over a number of engine test cycles, yielded conversion efficiencies anywhere between about 80 and 95 percent. The exhaust gas pressure drop over the in-use CRT filters was not reported in the study.

Field experience indicates a gradual increase in exhaust back-pressure levels due to the filter becoming loaded with ash, as shown in Figure 2-91.[168] Periodic reversing of the filter module is recommended as a means of cleaning the trap from these ash deposits. When operated with typical EU HD diesel oils of approximately 1.8 percent residual ash, the CRT needs to be reversed typically once per year.[165]
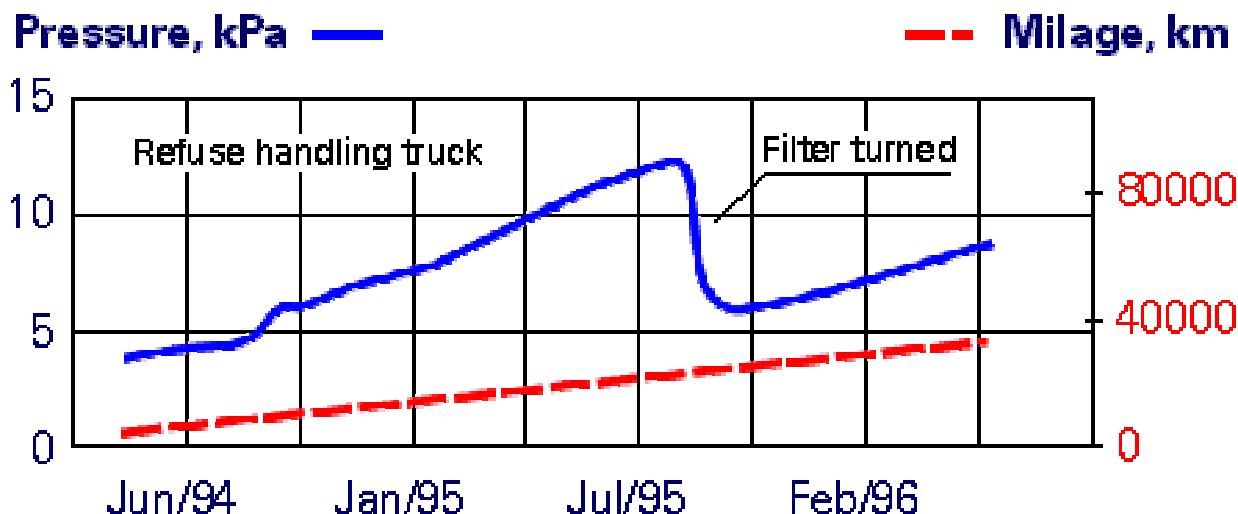
Figure 2-91. Exhaust back-pressure with CRT trap.

The first CRT filter study in North America was conducted by the New York City transit authority. In this study, 50 urban buses (25 with 1999 DDC Series 50 4-stroke engines and 25 with 1993 6V92 DDEC 2-stroke engines) were retrofitted and operated over an 8-month evaluation period using 30 ppm sulfur diesel fuel. The filters regenerated properly on the newer Series 50 engines, but experienced several instances of filter plugging on the older, 2-stroke 6V92 engines.[176] In-service exhaust temperature recordings from the Series 50 buses indicated that the exhaust temperatures were above 275° for 60 percent of the operating time. The filters maintained stable pressure drop levels with maximum readings of about 14 kPa (4 in Hg).[171,177] Published test data from heavy-duty retrofit applications indicate a fuel penalty of 1-3 percent, due to the increased system back-pressure. This is consistent with the 2 percent fuel economy penalty, as measured in laboratory by the DECSE program.[162]

Filter systems based on the two-stage CRT configuration have been also developed for new diesel passenger car applications. However, contrary to heavy-duty engine retrofits which can operate as totally passive systems (at least in some applications), light duty engines require some form of active regeneration support. Exhaust temperatures were evaluated on both the ECE+EUDC and the US FTP-75 cycles, as well as during real city driving, to determine the feasibility of CRT use. In all cases the temperatures were too low to sustain continuous filter regeneration.[174]

A prototype filter system for the Volkswagen D1 V10 5.0l engine (10 cylinder TDI passenger car engine, rated 230 kW at 4000 rpm) is shown in Figure 2-92.[178] The system includes two two-stage catalyst-filter units (one per exhaust bank) in the underfloor position. It relies on an active strategy, involving engine management and a close-coupled "warm-up" catalyst, to periodically increase filter temperature. At the time Volkswagen unveiled the engine, there was no decision whether this filter system would be commercialized.
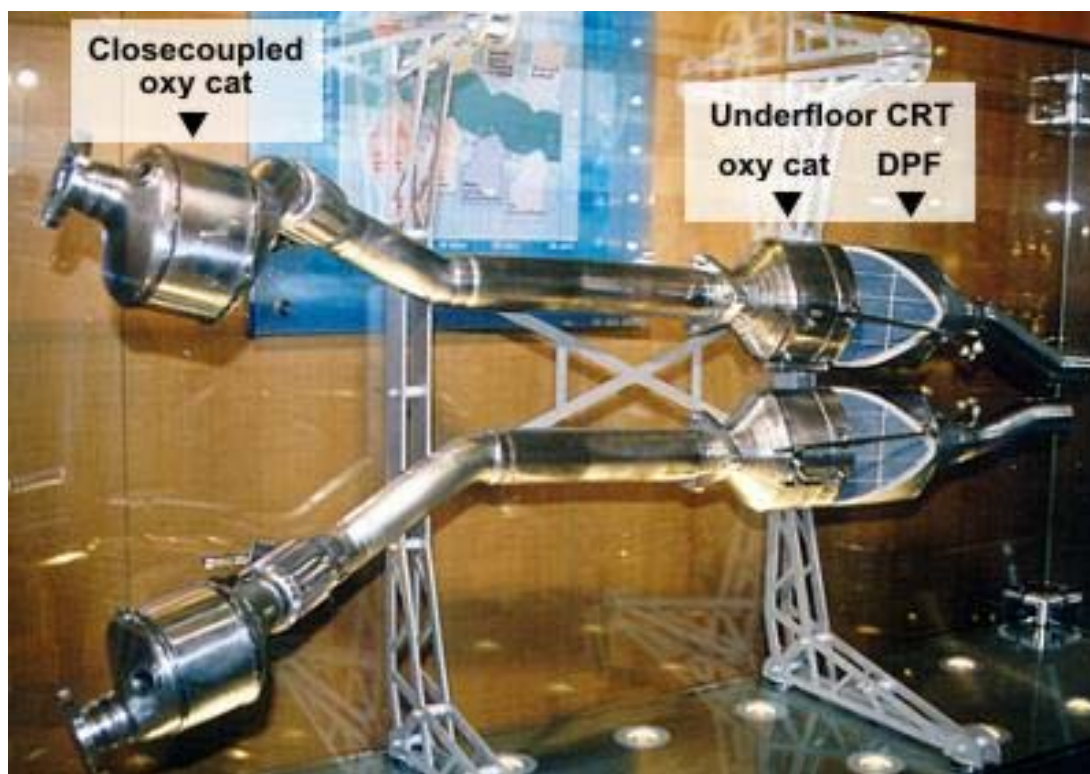
Figure 2-92. Prototype of light-duty CRT system.

C.6.3.7. SCRT System

A combination of the CRT filter with an urea-SCR (selective catalytic reduction) catalyst, termed SCRT, has been proposed to address the need for simultaneous reduction of PM and NO$_x$ emissions.[179] The CRT was positioned upstream of the SCR catalyst to enhance the SCR performance by increasing NO$_2$ content of the exhaust gas (this effect was discussed in the SCR catalyst section earlier).

It was shown that today's engines equipped with the SCRT system could meet the Euro 4/5 PM and NO$_x$ limits. The list of issues for future system optimization includes N$_2$O and ammonia slip, high exhaust gas pressure drop (up to 20 kPa), secondary PM emissions (presumably ammonium nitrate/sulfate), and system durability.

C.6.4. Traps With Fuel Additives

Fuel additives, also called fuel soluble catalysts, can be used in passive diesel trap systems to lower the soot combustion temperature and to facilitate filter regeneration. The most popular additives include iron, cerium, copper, and platinum. Many laboratory experiments and field tests have been conducted to evaluate the regeneration of various diesel filter media, e.g. the Nextel fibers, using additives. Cerium additive was utilized in a commercial trap system for diesel cars designed by Peugeot.

C.6.4.1. Fuel Additives

Metal based fuel additives were first studied as smoke suppressants and cetane improvers.[180] Several metals, including Ba, Ca, Fe, and Mn, have been found effective in lowering the amount of soot formed during combustion in both diesel and SI engines. This effect was explained by a combination of the following three mechanisms:

> - Ions or radicals of the alkali or alkaline earth metals used as additives remove particle precursors.

> - The ions or radicals inhibit the nucleation of particle precursors.

Many transition metals catalyze the oxidation of particulates at a later stage of the soot formation process. The most effective smoke suppressants, Ba and Ca, are believed to work primarily through the first two mechanisms.

Currently, the main interest in metal based fuel additives is related to diesel particulate traps. Numerous metal additives have been investigated as soot oxidation catalysts that would facilitate regeneration in passive diesel filter systems. Fuel additives used for that purpose are also called fuel soluble catalysts. As the additive is combusted in the engine cylinder, its metal component leaves the combustion chamber in the form of the corresponding metal oxide or other inorganic compound (e.g. sulfate). These compounds can form particles of their own or can be incorporated into diesel particulates. After being collected in the particulate filter, the catalytic metal is distributed throughout the diesel particulate phase and can effectively catalyze the oxidation of carbon particles.

The mechanism of trap regeneration is similar to that of a catalyzed filter, except the use of additives provides better contact between the catalyst and the carbon particles. This is probably why additive regenerated traps regenerate at somewhat lower temperatures than the catalyzed traps. However, even though fuel additive trap systems may have the lowest regeneration temperatures, they are not likely to provide the ultimate solution of the particulate problem, especially in light-duty applications. As illustrated in the following examples of filter systems, there are new "passive-active" approaches that support the additive-induced regeneration with some engine management measures in order to periodically increase exhaust gas temperature.

Although many papers have been published on diesel trap additives, there is little or no information on such issues as the actual interactions between the additive and diesel particulates, catalytic mechanisms, additive particle size and its distribution within the diesel particle phase.

Fuel additives are fuel-soluble organometallic compounds. Since the additive compound is destroyed by oxidation during the combustion process, its exact chemical formulation is, from the catalytic activity point of view, of limited importance. The additive formulation is, however, very important for its stability and miscibility properties. Organometallic compounds used for diesel trap additives that were reported in the literature include fatty acid soaps, acetyl acetonates, alcoholates, beta-diketonates, sulfonates, carbonates, carboxylates, dicyclopentadienes, and naphtenates.[181]

Tens of compounds of various transition, alkaline, and noble metals have been tested as fuel additives to facilitate diesel trap regeneration. The list of metals includes sodium, lithium, calcium, barium, manganese, iron, nickel, cerium, copper, lead, silver, vanadium, platinum, and more. For the purpose of diesel trap regeneration, additives are usually added to the fuel at concentrations from a few to about 100 ppm by weight of the respective metal. The choice of additive level depends on the activity of the particular additive, exhaust gas temperature, and the quantity and composition of particulate emissions. Generally, higher additive concentrations allow the trap to regenerate at lower temperatures. The disadvantages of high additive levels are (1) increased filter pressured drop due to the accumulation of ash and (2) higher operating cost.

Additive concentrations much higher than 100 ppm have been reported in several laboratory studies. Such high concentrations may have only academic importance and are not practical. Even the concentration of 100 ppm can result in significant pressure drop build-up in the filter due to accumulation of the additive ash and appears to be too high for practical purposes. Fuel additive for diesel trap regeneration which have successfully passed laboratory evaluations and are either commercial products or undergo field evaluations are listed below.

Table 2-20. Fuel additives for diesel filter regeneration.

Active Metal/Compound	Brand Name	Supplier
Iron (Fe/ferrocene)	Satacen	Octel (Pluto)
Iron - strontium (Fe/Sr)	Octimax 4800	Octel
Cerium (Ce)	Eolys	Rhodia
Platinum (Pt), platinum – cerium (Pt/Ce)	Platinum Plus	Clean Diesel
Copper (Cu)	-	Lubrizol†

† - Lubrizol copper additive is no longer commercially available. Lubrizol has exclusively licensed the Clean Diesel "Platinum Plus" additive for sale in Europe.

It should be kept in mind that commercial use of additives in different countries may require a formal approval or certification. Thorough health and biological studies are sometimes required by regulatory agencies to grant such approvals. In the USA, additives require an EPA registration to be legally sold for on-road use (with the exception of underground mining, no additive approval is required in the USA for off-road use). Not all products from Table 2-20 have received such registration.

The following is a list of potential drawbacks and unresolved issues that have to be addressed by designers of fuel additive regenerated diesel filter systems:

- ***The necessity of introducing the catalyst to fuel***. In most fuel distribution systems doping the fuel with additive is not practical. On-board automated dozing devices are being developed to introduce the additive directly to the vehicle's tank after the vehicle is fueled. However, such devices increase the system complexity and, in effect, turn passive traps into more complicated and expensive active systems.

- ***Ash deposits on the filter***. Most of the additive is trapped on the filter in the form of an inorganic oxide and/or salt. With time, it accumulates to considerable quantities. The ash deposits contribute to increased pressure drop.

- ***Ash emissions***. Additive ash that is not trapped, due to limited filtration efficiency or filter failure, is emitted to the atmosphere and may have adverse health or environmental effects. A formal approval or certification of additives is required by law in some countries.

- ***Impact on engine-out emissions***. Additives can improve or deteriorate the engine-out gaseous and particulate emissions. Various emission characteristics may be affected, such as PM size distribution. Additives may also create new secondary emissions.

- ***Impact on the engine or its components***. Some additives are known to cause fuel injector fouling. Generally, additives have to be tested for engine wear problems. For engine warranty reasons, the use of additives should be always approved by the engine manufacturer.

- ***Fuel stability***. Blending the additive with fuel may result in deposit formation, an increase in sedimentation from the fuel itself, and/or increased deposit formation when water is added to the doped fuel.

The importance of proper additive testing for its possible engine impact is best illustrated by an incident of additive-induced engine problems which was reported in Germany, where several 6 ton forklift trucks were equipped with a passive, additive regenerated, commercially available diesel particulate filter system.[182] The systems were installed on Deutz BF6M1012 engines, rated 85kW at 2200 rpm. After about 2000 engine hours, reduced power, increased smoke and other engine problems were reported. It was found that the additive caused severe injector fouling by oil-derived coke and magnetite compounds. As illustrated in the microscope photographs of the contaminated injectors shown in Figure 2-93, several injector holes are completely plugged by a thick layer of deposits. Actual additive levels in the fuel, as measured in the field, were found to be between 8 and 50 ppm.
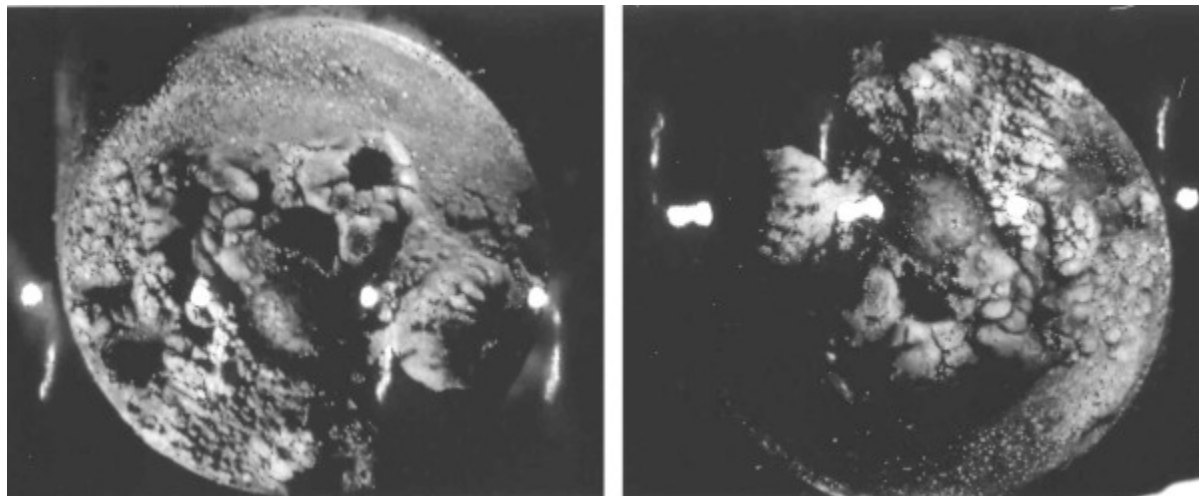
Figure 2-93. Contaminated fuel injector tips.

C.6.4.2. Catalytic Metals

Iron/Ferrocene: Iron, in the form of ferrocene (dicyclopentadienyl iron, $(C_5H_5)_2Fe$), has been commercially available as a combustion improver to increase fuel economy, primarily for bunker fuel in heating applications. It is also suitable as a diesel trap additive, as demonstrated by several studies.[183,184] A ferrocene-regenerated trap system for industrial forklift trucks has been commercially offered in Germany by GfA. The molecular structure of ferrocene is schematically shown in Figure 2-94. The molecule includes a central iron atom bonded with two symmetrical cyclopentane rings.
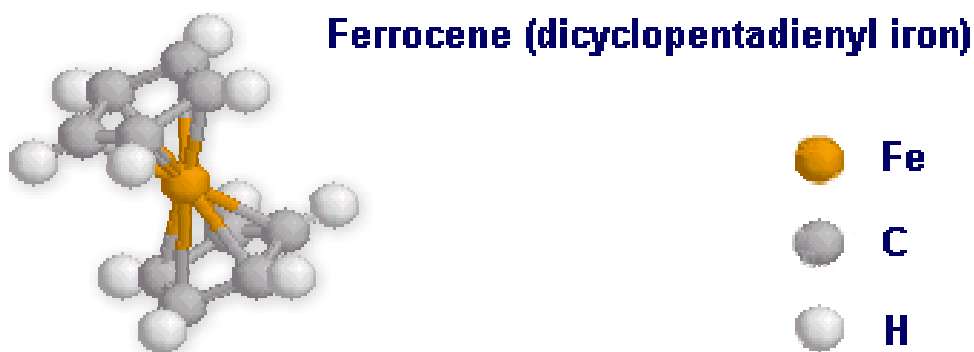
Figure 2-94. Molecular structure of ferrocene.

Several ferrocene derivatives that have been manufactured as fuel economy improvers are listed in Table 2-21.

Table 2-21. Ferrocene derivatives used as fuel additive.

dicyclopentadienyl iron	di(methylcyclopentadienyl) iron
di(ethylcyclopentadienyl) iron	methylferrocene
ethylferrocene	n-butylferrocene
dihexylferrocene	phenylferrocene
m-tolylferrocene	didecylferrocene
dicyclohexylferrocene	dicyclopentylferrocene

For the purpose of diesel trap regeneration, ferrocene levels of about 18 ppm by weight as Fe (60 ppm wt. ferrocene) have been recommended by additive suppliers. Fe levels of 36 ppm by weight (120 ppm ferrocene) were used in the VERT program for retrofitting of construction diesel engines with passive, additive-regenerated systems.[183]

Fe/Sr: A new iron based, non-ferrocene additive has been introduced by Octel. The additive has been specifically designed as a diesel trap additive and includes iron and strontium as active components. According to the manufacturer, the required additive dosage is between 10 and 20 ppm by weight of combined metal (Fe + Sr).[185]

Cerium: Cerium-based diesel filter additive has been developed by Rhodia (former Rhone-Poulenc). It is commercialized under a brand name Eolys. The additive has been tested with diesel filters in urban bus, car, and other applications, primarily in Europe. The advantages of cerium claimed by Rhodia include its biological inertness and non-toxic character. An improvement in engine-out emissions is also attributed to cerium.[186]

The Ce additive was proven in several studies to be effective in diesel trap regeneration and compatible with filer media.[183,184] Additive dosage levels used in projects where heavy-duty diesel engines were retrofitted with passive, cerium regenerated systems were in the range of 100-120 ppm by weight Ce, which tends to be higher than additive levels reported for iron/ferrocene.

A study on the compatibility of metal oxide ashes with diesel filter materials found that cerium ash had less deteriorating effect on cordierite wall-flow substrates than iron based ashes.[187]

Platinum: Platinum additive was introduced under the brand name Platinum Plus by Clean Diesel Technologies (CDT). According to the manufacturer, the Pt additive is suitable for both decreasing the engine-out emissions and regenerating diesel traps. A study on the activity of Pt fuel additives was conducted at the University of Delft.[188] It was found that a synergistic effect exists between Pt and Ce, when used as diesel trap additives. Furthermore, the lowest balance temperatures were seen on traps that were pre-catalyzed with Pt in conjunction with a small dose of Pt/Ce fuel additive. Minimum balance temperatures for different trap/additive systems, as determined on a laboratory Lister Petter LPW2, 2 cylinder, DI, NA, water-cooled engine, are listed in Table 2-22. The minimum balance temperature was defined as the minimum temperature at which a stable pressure drop level could be achieved at a steady-state engine operation. The corresponding pressure drop was 15 - 20 kPa (60 - 80 "H2O). 500 ppm sulfur fuel was used in all experiments.

Table 2-22. Balance temperature for different TRAP/Additive systems.

Additive	Concentration, ppm wt.	Filter	Temperature, K	Temperature, °C
None	-	EX-80	810-830	537-557
None	-	Pt EX-80	690-700	417-427
Cerium	100	EX-80	705	432
Platinum/Cerium	0.5 - 5	Pt EX-80	600	327
Platinum/Copper	0.5 - 5	Pt EX-80	620	347
Platinum/Iron	0.5 - 22	Pt EX-80	630	357

It was illustrated by a series of laboratory reactor experiments that NO chemistry played an important role in the overall process. However, no clear explanation exists as to the mechanism of the synergistic effect between Pt and Ce or to the superior performance of traps with supported platinum catalyst. A definite advantage of the Pt/Ce additive would be its low dosage level, apparently as little as 5 ppm, minimizing the fouling effect of the additive ash on traps.

It should be kept in mind that performance data on Pt additives was generated in laboratory conditions. The advantages of this promising product, including its high activity at low dosage level, have to be confirmed by evaluations under field conditions.

Copper: Copper based additive for trap regeneration was developed and extensively tested by Lubrizol. The copper additive was also found to be the most effective of the additives tested by the VERT program. Additive levels of about 60 ppm by weight Cu were used in the VERT study. The copper additive, however, caused some negative effects on engine-out emissions. The biggest concern was the generation of secondary emissions of dioxins and furanes from engines equipped with Cu-regenerated traps.[189] Other additives, including Fe and Ce, were not producing dioxins or furanes. These health concerns have made the copper additive less attractive. The copper additive was also reported to cause severe fouling of fuel injectors. Gold-plated injectors were developed in an attempt to solve this problem.[189]

C.6.4.3. Peugeot Filter System

PSA Peugeot Citroen developed a diesel particulate filter system that went into serial production in 2000.[190] Peugeot used the filter as a standard component on its model DW12 TED4, 2.2 liter, 98kW, common rail, passenger car diesel engine. The filter is designed to reduce particulate emissions from diesel fueled cars to levels required by the year 2005 EU emission standards for light duty vehicles, i.e. 0.025 g/km.

The filter system utilizes a fuel additive to lower the soot combustion temperature to support the regeneration. Since the system also includes elements of active engine strategy to periodically increase the exhaust gas temperature, it hardly meets the definition of a passive trap system. The PSA trap system is a textbook example of a system approach to diesel emission control, where (1) a new technology low emission diesel engine, (2) elements of active engine strategy and (3) exhaust gas aftertreatment are combined together to achieve the emission target.

The Peugeot system includes a porous silicon carbide trap and an oxidation catalyst upstream of the filter. Cerium based fuel additive (Eolys by Rhodia) is used to lower the combustion temperature of soot, allowing the filter to regenerate at temperatures below 450°C. This temperature, however, is not reached during regular operation of the car. Therefore, the system includes active means of increasing the exhaust temperature in order to trigger regeneration.

The regeneration of the filter is controlled by the common rail injection system, which increases the exhaust gas temperature through a combination of two effects:

- Multiple post-injections of fuel in the expansion stroke cause exhaust temperature to rise by 200 to 250°C.

- Complementary post-combustion, generated by the oxidation catalyst upstream of the filter, deals with the unburnt hydrocarbons resulting from the post-injection. The temperature can be increased by more than 100°C.

The combination of both effects increases the exhaust gas temperature to about 450°C. Filter regeneration occurs periodically every 400-500 km, depending on the driving pattern of the particular vehicle.

The additive is stored on vehicle and automatically dozed. When the vehicle fuel tank is topped up, the fuel additive system injects the required quantity of the additive. For a full tank of 60 liters the system will inject 37.5 ml of the solution containing 1.9 g of ceria. This ratio corresponds to a Ce concentration in fuel of 25 ppm by weight. The additive reservoir's 5-liter capacity gives a range of 80,000 km. After the 80,000 km the additive must be replenished and the filter cleaned from the additive ashes by flushing with pressurized water.

A combined fuel economy penalty of up to 5 percent, depending on the vehicle driving pattern and frequency of regeneration, is associated with the increased pressure drop in the filter and with the post-injections of fuel.

C.6.4.4. Nextel Filters with Fuel Additives

Additive Comparison: A study on the compatibility of the Nextel fiber fibers with fuel additives (or fuel soluble catalysts) regeneration was undertaken by 3M Company.[184] The study included laboratory filter regeneration tests, engine bench durability tests, and field tests with some of the additives. The work was targeted on heavy-duty bus and truck engines. Three additives based on the following active metals were evaluated:

- copper (Cu)

- iron (Fe)

- cerium (Ce).

Filter regeneration using these three additives was compared on a Cummins NTC-350 engine under identical test conditions (Figure 2-95). Media dimensions of the evaluated wound fiber cartridge were 140 mm diameter x 1270 mm length. The engine was operated on an automated speed/load cycle to allow filter loading (light load) and also to force regeneration on each cycle (high speed and load). The curve profiles in Figure 2-95 reflect these loading and forced regeneration segments of the test cycle. Additive dose rates listed in the graph are all on metal basis.
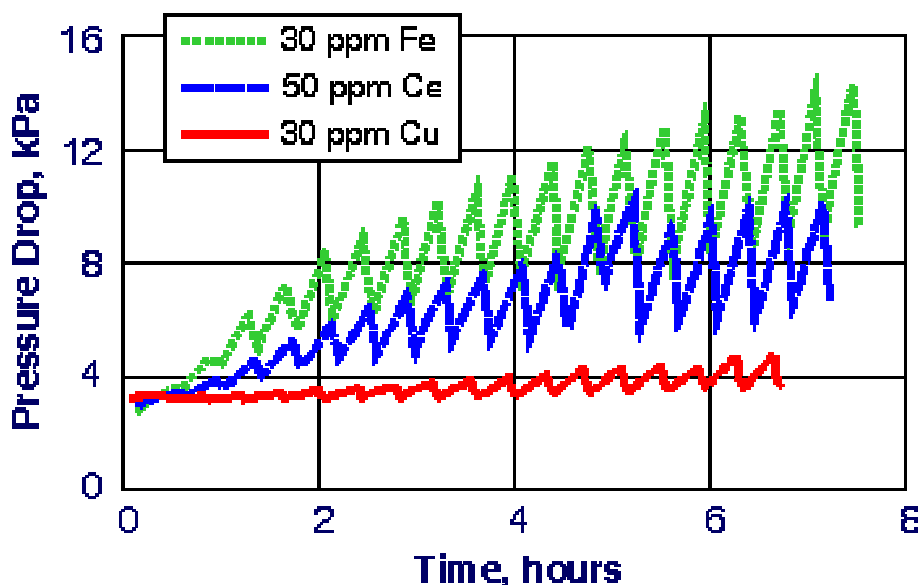
Figure 2-95. Regeneration behavior with FE, CE, and CU additives.

The above results indicate that the copper-based additive promotes the highest regeneration rate resulting in the lowest average pressure drop in the filter. Iron promoted regeneration at the slowest rate while cerium was in-between Cu and Fe. Additional laboratory testing revealed an important difference between the regeneration behavior induced by copper and that with Ce or Fe. When tested at constant exhaust gas temperature, the copper additive had a tendency to promote periodic soot built-up and regeneration cycles. Soot load in the filter was increasing up to a certain level, and then ignited and rapidly combusted releasing heat and resulting in high temperature peaks. The cerium and iron additives, on the other hand, promoted continues filter regeneration. During the continuous regeneration, filter operates under balance conditions where the amount of soot entering the filter equals to that which is being oxidized in the filter. There is no rapid combustion and no high temperature spikes in the filter media.

Copper Based Additive: Further laboratory tests conducted with the copper based additive revealed that the Nextel filters exhibited high copper ash collection efficiency of 95-99 percent but no fiber deterioration was observed in the lab. During the subsequent field testing, however, it became apparent that filter systems were failing after about 30000 km of use. Visible smoke was observed after the filter and investigation revealed a drop in filtration efficiency from 90 to about 50 percent.

Upon disassembly of the filters, it was discovered that copper ash produced a sticky coating on the filter media obstructing filter passages and bonding fibers together. Analysis of fibers confirmed that high temperatures during regeneration resulted in glazing of the copper and oil ash, and bonding the fibers together. The matrix of fiber and glassy ash was brittle, leading to fiber damage by the thermal, mechanical, and vibration stresses experienced during operation.

It was concluded that ceramic fiber wound filters are not compatible with copper-based fuel additive.

Iron Based Additive: Laboratory evaluations of the iron additive were conducted on a 1994 EPA and CARB certified, 5.9L DI, turbocharged, air-charge-cooled diesel engine, rated 119 kW at 2500 rpm. A concentric tube pack filter was used including three wound fiber cartridges nested one inside another. The engine test cycle was composed of repeated 1-hour segments. Each segment included 20 iterations of a simulated urban bus driving cycle (54 percent duty cycle based on rated speed fuel rate) and 2 steady-state sections (7 minutes at torque peak and 8 minutes at rated speed conditions). The dose rate of iron additive during the test was about 4 ppm. The average exhaust gas temperature was increasing over the 1000-hour test from about 380°C to 440°C as a result of increasing exhaust pressure. The average filter pressure drop and the total mass (ash + soot) accumulated in the filter are plotted versus time in Figure 2-96.
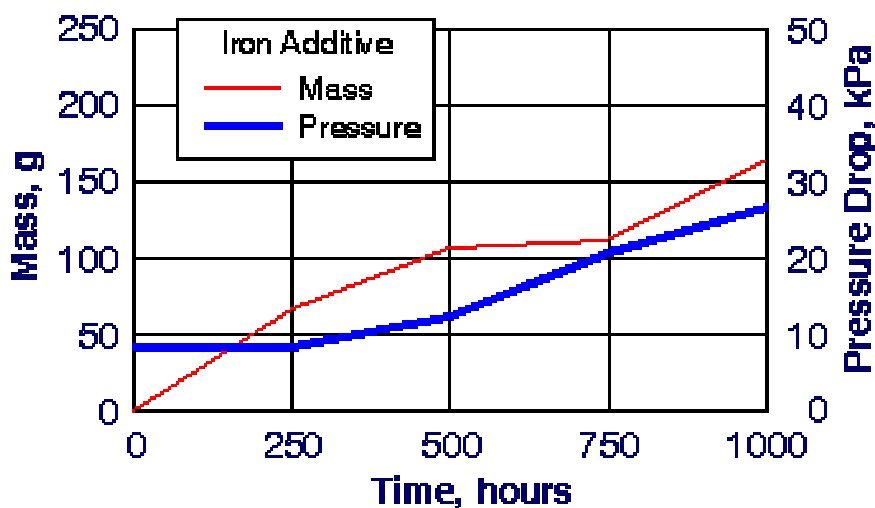
Figure 2-96. Total collected mass and pressure drop (Fe Test).

The following observations were made during the 1000-hour test with iron fuel additive:

- After some initial period, recorded soot filtration efficiencies were higher than 90%. Slightly higher efficiencies were observed during steady state conditions than during transients.

- The filter regenerated properly. There was no damage or deterioration to the fibers. There was no evidence of material sticking to the fibers in photomicrographs taken after tests.

- Ash analysis indicated that a phase change (glazing) occurs at 900°C. Since the ash in the filter was not glazed, regeneration temperatures must have been below that level.

- Most of the iron ash was retained in the filter (87.6 percent collection efficiency of Fe_2O_3 was measured).

- Oil and iron ash mass balance calculations confirmed that the increase of filter mass and its pressure drop (beyond some initial period of less than 250 hours) was due to the oil and iron ash accumulation (Figure 2-96). Analysis revealed that 43 percent of total non-combustible deposit found in the filter was derived from the iron additive.

- A 14 percent increase in engine-out particulate emission due to increased exhaust pressure was recorded over the 1000-hour test.

- A 0.85 percent increase of fuel consumption was recorded during the test.

Field testing of Nextel filters with iron additives commenced on fifteen city buses in Bucharest, Romania. All of the buses were powered by RABA-MAN D2156 H6U engines. Some of the buses were equipped with a concentric tube pack filter while others used assemblies of eight non-concentric Nextel cartridges. The additive dose was 30 ppm Fe (100 ppm ferrocene). Over 17 months of test, the fleet buses accumulated between 48000 and 120000 km (average 80000 km per bus). One of the systems failed mechanically in that time period. Other systems maintained their performance as indicated by smoke number measurements. The average system performance is listed in Table 2-23.

Table 2-23. Average vehicle performance.

Smoke number, no filter	5.1
Smoke number with filter	1.2
Pressure drop across filter	6 kPa
Filter inlet temperature	300°C
Filter outlet temperature	260°C
Noise level, muffler - no filter	87.5 dB(A)
Noise level, filter - no muffler	88.0 dB(A)
Increase in fuel consumption	6%

*Cerium Based Additive***:** Cerium based additive was evaluated under laboratory conditions similar to those used with the iron testing. The additive dose rate was higher than that in the Fe test, and amounted to 12 ppm. Exhaust temperature increased during the test from 380 to 470°C. Pressure drop and mass curves taken during a 700 hour test are shown in 2- 97. A faster pressure build-up was observed than that in the test with iron.
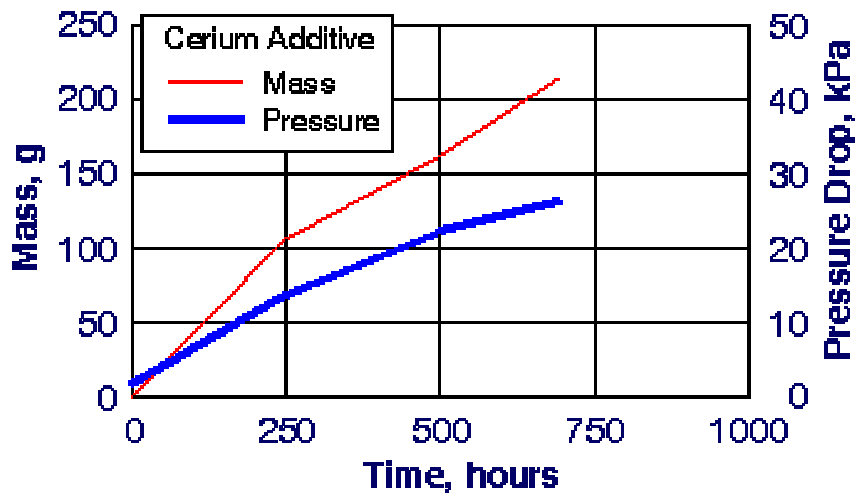
Figure 2-97. Total collected mass and pressure drop (Ce Test).

The following observations were made during the 700-hour test with cerium based fuel additive:

- After the initial period, soot filtration efficiencies were higher than 90 percent.

- The filter regenerated properly and no damage or fiber deterioration occurred. Fiber photomicrographs showed layers of ash material flaking from the fiber.

- Ce-oil ash analysis indicated that the glazing process occurs at 900°C, similarly to the Fe ash. No glazed ash was found in filters, so the regeneration temperatures must have been below that level.

- Most of the cerium ash was retained in the filter (90.5 percent collection efficiency of CeO_2 was measured).

- The increase of filter mass and its pressure drop (beyond some initial period of less than 250 hours) was due to the accumulation of ash from oil and cerium additive (Figure 2-96). Analysis revealed that 55 percent of total non-combustible deposit found in the filter after tests was derived from the cerium additive.

- A decrease in engine-out particulate emission of 21percent was recorded over the 700-hour test, despite the increased pressure in the exhaust system.

- A 4.7 percent increase of fuel consumption was recorded during the test.

C.7. Non-Thermal Plasma as an Auxiliary Exhaust Emission Control Device

Non-thermal plasma (NTP) discharges in exhaust gas have been studied as a potential method to reduce NO_x and PM emissions in diesel exhaust as well as NO_x and cold start hydrocarbons in lean gasoline exhaust. Vehicle exhaust gases, both diesel and gasoline, undergo chemical

changes when exposed to plasma. Logically, oxidation processes dominate in the presence of oxygen. These reactions include oxidation of hydrocarbons, carbon monoxide, and, to a degree, diesel particulate matter. Nitric oxide (NO) can be oxidized by plasma to NO_2. The oxidation properties of plasma have been utilized in the treatment of flue gases from power plants.[191] In the power plant flue gas treatment the purpose of the plasma is to oxidize NO to NO_2 and subsequently to nitric acid. The desired products, in the form of ammonium salts, are then obtained by reacting the formed acid with ammonia. Industrial plasma systems have also been demonstrated for VOC removal.

Obviously, this method of NO_x removal is not applicable for trucks or cars. The objective in the plasma treatment of exhaust gases from internal combustion engines is the reduction, as opposed to oxidation, of NO_x. Contrary to some earlier literature reports, there is now a wide consensus that plasma alone, due to its oxidizing character, is not a viable NO_x control method. However, combinations of plasma with catalysts, referred to as "plasma-assisted catalysts" or simply "plasma catalysts", have been suggested for NO_x reduction. Plasma is believed to show potential to improve catalyst selectivity and removal efficiency. Current "state-of-the art" plasma catalysts have efficiencies comparable to those of active deNOx systems, removing about 50 percent of NO_x at a fuel economy penalty of less than 5 percent.[192]

In the case of diesel exhaust a removal of particulate matter emissions would be also a valuable benefit of plasma systems. Plasma systems have been shown to be capable of reducing of diesel particulate matter by low temperature oxidation. It is not currently clear whether the NO_x and PM control functions by plasma can be combined in one device, i.e., if NTP reactors can be designed for the simultaneous control of NO_x and PM.

An increasing number of research reports are published in the literature increasing our understanding of plasma chemistry in the engine exhaust gases. However, this technology has still a novel character and published results need to be evaluated with caution. Since many studies are conducted in small scale laboratory experiment, as opposed to a full-flow engine experiment, erratic interpretation of data is frequently suspected. It is very easy to overlook a formation of unidentified chemical compounds in the plasma or to confuse adsorption and storage of material in the test equipment with its steady-state removal. For vehicle plasma applications, it is very important to make a distinction between NO removal by chemical oxidation and NO removal by chemical reduction. The desired overall process is chemical reduction to benign products, such as nitrogen and oxygen. In plasma processing literature many authors use the term "NO reduction" even when the NO removal is accomplished by oxidation to NO_2 and nitric acid. It is not sufficient for a plasma experimental work to record a decrease of the NO or NO_x concentration. Possible reaction products may include many other nitrogen species which may be not acceptable. Several of these by-products may be also difficult to detect in the laboratory setup. Besides nitrous and nitric acids these products may include nitrates, nitrites or organonitrites which can be deposited on reactor walls, on particulates, or on the pellets material if a packed bed reactor is used. Even if chemical reduction of NO dominates, the products may include nitrous oxide N_2O which, although not a regulated emission, is not an acceptable product. Commercialization of non-thermal plasma technology for emission control from mobile sources requires significant advancements and much more development work. The plasma may or may not become a viable choice for lean NO_x or PM removal systems.

C.7.1. Non-Thermal Plasma

What Is Plasma: Plasma is a gas consisting of positive and negative charges that has a tendency to remain overall electrically neutral over large length scales. It is composed of free electrons, ions, radicals, atoms, and molecules in various states of excitation. Plasma is divided into "thermal" or "hot" plasma and "non-thermal" or "cold" plasma. In the thermal variety the kinetic energy (temperature) of charged particles and the kinetic energy (temperature) of the background gas are similar. In this type of plasma the electrons energy is transferred through collisions to other components of the gas stream. Because of the high temperatures, a considerable amount of heat must be added to the system to maintain thermal plasma. An example of thermal plasma is the electrical arc discharge.

In the non-thermal plasma electrons have a kinetic energy higher than the energy corresponding to the random motion of the background gas molecules. The intent of using non-thermal plasma is to selectively transfer the input electrical energy to the electrons that would generate free radicals through collisions and promote the desired chemical changes in the exhaust gas. These reactions can be accomplished at a fraction of the energy that is required in the thermal plasma system. An example of non-thermal plasma is the gas filling a fluorescent tube. Its temperature is only about 40°C but the temperature of free electrons in the system exceeds 10,000°C.

Non-thermal plasmas are favored by low pressure systems. At ambient pressure high local electrical fields are needed to maintain non-thermal plasma. However, there is also a maximum field beyond which non-thermal plasma cannot be maintained and will develop a thermal plasma discharge. The highest electric field that can be applied while still maintaining non-thermal plasma is known as the *electrical breakdown threshold*. Under atmospheric pressure conditions in an N_2 or air discharge, the electrical breakdown threshold corresponds to an electron mean energy of around 4 eV. Non-thermal plasma reactors typically operate in the regime where the average kinetic energy of the electrons is in the 3-6 eV range.

Typically, space electrical charges build up in the NTP, which cancel the effect of the external electrical field. Therefore, in order to maintain a continuous NTP discharge, the reactors are powered by either alternating current (AC) of pulse generators. Ultra short pulse supplies (less than 50 ns) were reported to increase the breakdown threshold and, as a consequence, the energy transfer to the gas.[193] However, current technology to produce ultra short pulses is inefficient. Stationary systems use readily available 60 Hz power that, due to large and heavy high voltage transformers, is not practical for mobile applications. The ozonator industry uses 1.2 kHz transformers, which are readily available and have been adapted in some engine studies.[194]

C.7.2. Plasma Generators

Non-thermal plasmas can be produced in a number of ways including a variety of electrical corona discharges, radio frequency discharges, microwave discharges, or electron beams. The following NTP technologies are considered for emission reductions in engine exhaust streams:[193]

-Corona Discharge

-Surface Plasma Discharges

-Dielectric Barrier Discharges

-Dielectric Packed Bed Reactor

-Electron Beam Reactor

Corona Discharge: Corona discharge (2-98) is the simplest type of plasma generator. A feature of the corona discharge, which differentiates it from the other discharges, is that no dielectric is involved. Instead, an electron avalanche is initiated from a sharp metallic surface where the radius of curvature is small. The electric field has to be pulsed in order to prevent the plasma from going into the thermal mode and forming an arc. The electric fields in corona reactors are in the order of 50 kV/cm.
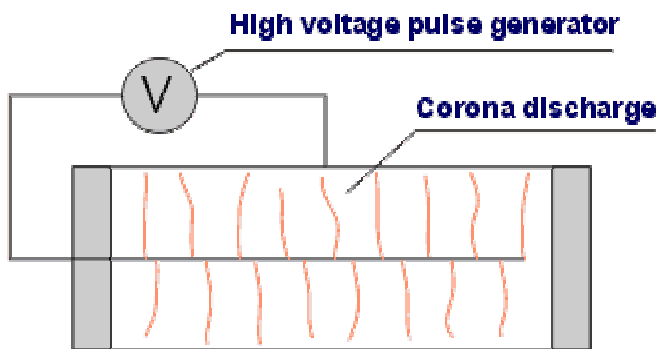
Figure 2-98. Corona discharge.

Surface Plasma Discharges: In this configuration, shown in Figure 2-99, the electric fields are parallel to the surface. One of the electrodes is attached to one side of a dielectric. The other electrode is placed at the other side but does not cover the dielectric completely. The plasma is created adjacent to this dielectric surface which is in contact with the gas. In operation, the surface plasma covers the entire dielectric surface during the pulse. A feature of this discharge is that after a few nanoseconds charge starts to build up at the dielectric surface, which has the effect of reducing the electric fields outside the dielectric, eventually extinguishing the discharge.
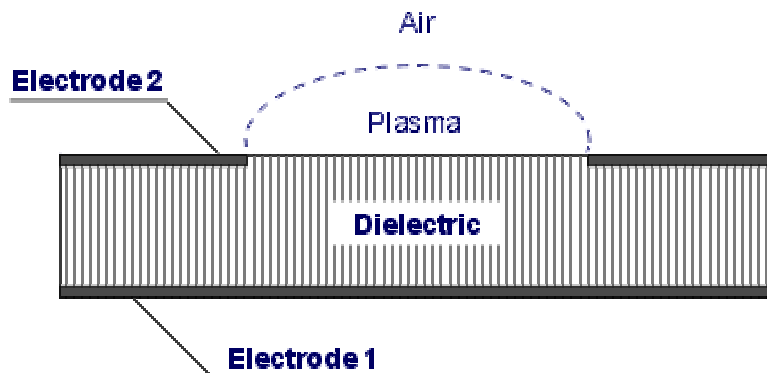
Figure 2-99. Plasma surface discharge.

Dielectric Barrier Discharges (DBD): These discharges are distinct from the surface discharges in that one of the electrodes is detached from the dielectric. Similarly to the corona discharges, small scale electron streamers are formed. When the electric field is perpendicular to the dielectric, streamers form with a density of about 100/cm^3. After several nanoseconds of operation, space charge builds up on the dielectric surface, locally cancelling the externally applied electric field and eventually extinguishing the discharge. In the DBD mode of operation, the threshold electric field is relatively low and low energy electrons are formed.
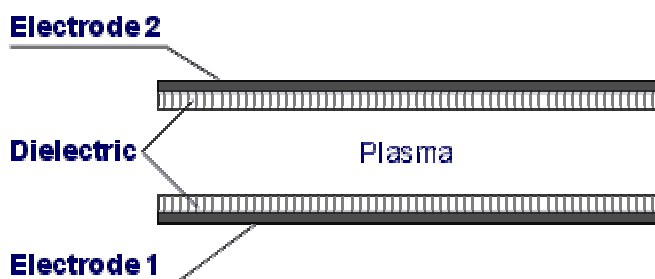
Figure 2-100. Dielectric barrier discharge.

DBD reactors can be also configured as concentric cylinders (similar to the corona reactor, but with surfaces coated with a dielectric layer) or as arrays of alternating positive and negative tube-shaped, dielectric coated electrodes. The parallel plate architecture, however, features the most simple and cost effective design. In a comparative study, a parallel plate reactor of 1 mm gap distance and 0.5 mm dielectric barriers provided the best balance between the performance and the exhaust gas pressure drop.[195]

A big advantage of the parallel plate geometry is the possibility to stack plates together to build larger reactors with higher power deposition to the gas. The alternating positive and negative electrodes in this design must have a dielectric layer on each side. A prototype of such stacked reactor has been built by Delphi.[194] Alumina plates, as used in the electronic industry, were selected as the dielectric barrier. The conductive electrode was "inked" onto the alumina using an Ag/Pd ink and covered with another alumina plate. A number of such plates were stacked on top of each other using 1 mm thick spacers between plates along two

opposite edges of the structure. The plate stack was glued together using high temperature glass encapsulant, wrapped with ceramic wool and stuffed into a stainless steel can. A full flow system for a 2 liter Opel diesel car was powered by a 3000 VA transformer of 6 kV output at 1.2 kHz.

Dielectric Packed Bed Reactor: In this configuration the dielectric in the form of small pellets is placed between electrodes. The pellets can be spherical, pebble-shaped, or other shape chunks. As a consequence of Gauss's law and the difference in dielectric constant between the pellets and the surrounding gas local electric field enhancements are observed outside the dielectric. A cylindrical configuration of the packed bed reactor is shown in Figure 2-101. Another configuration where pellets bed is placed between two flat electrodes is also possible.
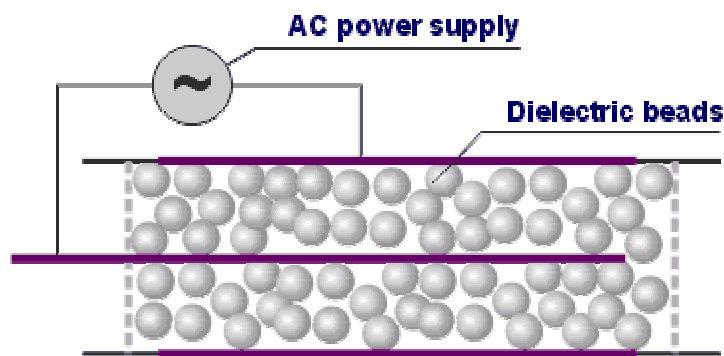
Figure 2-101. Packed bed reactor.

The advantages of the packed bed reactor include its simplicity and the possibility of using catalyst pellets which makes this type of reactor a possible choice for plasma-catalyst systems. The disadvantages of the packed bed are high pressure drop and attrition of the pellets.

Electron Beam Reactor: An electron beam is formed in a separate generator, such as a cathode tube, and injected into the exhaust gas stream. The energy of electrons can be much higher in the e-beam reactor than in the other reactors. The electron energy can be also better controlled, resulting in improved gas phase reaction efficiency. Disadvantages of the e-beam reactor are the need of special hardware (the electron generator) and poor efficiency in transferring the electrons into the gas.

C.7.3. Energy Efficiency

One of the critical issues in the use of plasma is the consumption of electrical energy. The overall efficiency of an NTP reactor can be divided into the following two components: (1) electrical conversion efficiency and (2) chemical processing efficiency. The electrical conversion efficiency refers to the efficiency for converting the input electrical power into the power deposited by electrons into the plasma. The chemical processing efficiency refers to the amount of pollutant removed or decomposed for a given amount of energy deposited into the plasma. The latter can be expressed in terms of the specific energy consumption in such units as electron volts (eV) per molecule of NO_x or grams of NO_x per kWh. Obviously, the

chemical processing efficiency is of fundamental importance and must satisfy user requirements before high electrical efficiency reactors are constructed.

Energy efficiencies reported by different studies vary greatly, depending on the reactor design, its operating parameters, targeted chemical processes, and, in the case of plasma-catalyst systems, on the catalyst formulation and configuration. A number of ideas are being pursued to improve the efficiencies of NTP reactors:

- Optimization of the electrode structure of the plasma reactor -- to increase the electrical conversion efficiency by minimizing energy losses. In the case of the parallel plate DBD device, the main electrical losses are related to the heating of dielectric barrier and to surface streamers.

- Optimization of the voltage wave form applied to the reactor -- to control various operation parameters, such as the electron energy.

- Optimization of plasma catalysts -- to take advantage of heterogeneous reactions.

It is customary in plasma research to express the amount of energy consumed by plasma devices relative to the amount of treated gas. This energy, often referred to as the *energy deposition* or *energy density*, is expressed in units of Joules per standard (STP: 101.325 kPa, 0°C) liter of gas and commonly abbreviated as J/L.

For those who specialize in engine and emission control technologies, the unit of J/L sounds fairly abstract. To better understand the energy requirement of plasma devices, it should be related to more common terms, such as the engine power output and the fuel economy penalty. It can be assumed that the diesel engine produces about 1.4 liters (STP) per second of exhaust gas per 1 kW of its output power. If so, the energy deposition of 10 J/L is equivalent to 1.4 percent of the engine rated power. In order to generate that amount of electricity, the engine will experience a certain fuel economy penalty. To estimate the fuel cost of electrical energy, one has to assume the conversion efficiency of the vehicle's alternator and the efficiency of the power supply from the typical 12 V to the high plasma voltage. Since the combined efficiency of these devices is about 70 percent, the cost of the electrical energy at 10 J/L is equivalent to approximately 2 percent fuel economy penalty. Plasma processes that use less than, say, 20 J/L of electrical energy may be therefore considered realistic. Processes that use up to some 30-40 J/L may be realistic, provided a progress in the NTP reactor efficiency is made. Many NTP devices that have been studied use much higher energy depositions, sometimes in excess of 100 J/L. The importance of these processes appears to be purely academic.

C.7.4. Chemical Reactions

Plasma Chemistry: A number of products have been detected in plasma-treated diesel exhaust gases, including a mixture of nitrogen oxides and acids, CO, aldehydes, and ozone (O_3). If the treated gas contains propene, often introduced to laboratory systems as a representative HC, formic acid, formaldehyde and acetaldehyde have been identified among the products. The underlying chemistry is not well understood. The following set of reactions represents a probable hypothesis rather than proven mechanisms. There are also numerous other reactions that are possible, but are believed to be less likely than the reaction pathways

presented below. The reactions apply to soot-free exhaust gas. The presence of diesel PM has been shown to influence the plasma chemistry, but the chemical mechanisms remain even more obscure. Some discussion is given in the section on the plasma treatment of diesel PM.

The chemical processes are initiated via electron induced dissociation of oxygen:

$$O_2 + e \rightarrow O + O + e \qquad (1)$$

The electron energy range in NTP reactors, typically at 3-6 eV, corresponds to a maximum production of oxygen radicals in air or exhaust gases, reaction (1). This is why NTP reactors are effective ozone generators:

$$O_2 + O \rightarrow O_3 \qquad (2)$$

Oxygen atoms are also very effective in oxidizing NO to NO_2. In the absence of hydrocarbons, the efficiency of NO_2 production, Eq.(3), is reduced by the reverse reaction (4), and also by the conversion to acids, reactions (5)-(6).

$$NO + O \rightarrow NO_2 \qquad (3)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (4)$$

$$H_2O + e \rightarrow OH + H + e \qquad (5)$$

$$NO_2 + OH \rightarrow HNO_3 \qquad (6)$$
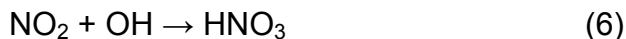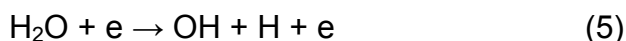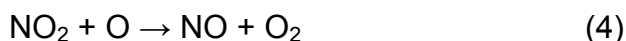
Hydrocarbons are attributed an important role in plasma. In the presence of hydrocarbons, the efficiency of NO_2 production is greatly increased. A possible explanation is that HCs act as a sink for O atoms and OH radicals. The resulting products react with O_2, to form peroxy radicals (HO_2), which further convert NO to NO_2. These processes are illustrated by Eq.(7)-(12), with propene as the example hydrocarbon species.

$$C_3H_6 + O \rightarrow C_2H_5 + HCO \qquad (7)$$

$$C_3H_6 + O \rightarrow CH_2CO + CH_3 + H \qquad (8)$$

$$C_3H_6 + O \rightarrow CH_3CHCO + H + H \qquad (9)$$

$$HCO + O_2 \rightarrow CO + HO_2 \qquad (10)$$

$$H + O_2 \rightarrow HO_2 \qquad (11)$$

$$NO + HO_2 \rightarrow NO_2 + OH \qquad (12)$$
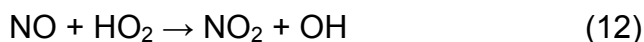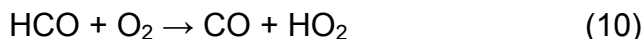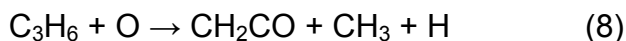
The hydrocarbons may also react with the OH radicals. This reaction provides a second method of promoting the NO/NO_2 shift, which, under the temperatures in engine exhaust gases, may become predominant, Eq.(13)-(15):

$$C_3H_6 + OH \rightarrow C_3H_6OH \qquad (13)$$

$$C_3H_6OH + O_2 \rightarrow C_3H_6OHOO \qquad (14)$$

$$C_3H_6OHOO + NO \rightarrow C_3H_6OHO + NO_2 \qquad (15)$$
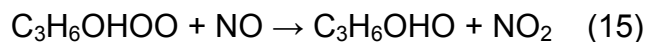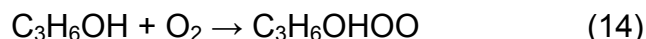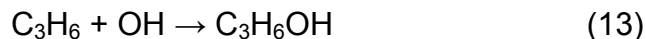
The produced alkoxy radical, Eq.(15), may decompose to acetaldehyde and CH_2OH, Eq.(16), which, in turn, may react with oxygen to formaldehyde:

$$C_3H_6OHO \rightarrow CH_3CHO + CH_2OH \qquad (16)$$

$$CH_2OH + O_2 \rightarrow HCHO + HO_2 \qquad (17)$$
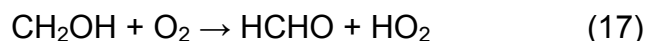
Finally, the acetaldehyde may react with OH radicals to formic acid, which may be broken down to such products as CO, CO_2, and H_2O.

$$CH_3CHO + OH \rightarrow HCOOH + CH_3 \qquad (18)$$

$$HCOOH + OH \rightarrow CO_2 + H_2O + H \qquad (19)$$

$$HCOOH + OH \rightarrow CO + OH + H_2O \qquad (20)$$

$$HCOOH + O \rightarrow CO + OH + OH \qquad (21)$$
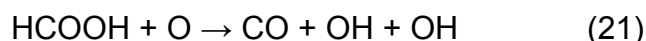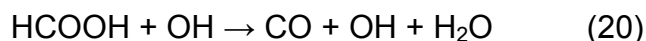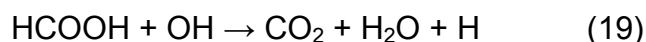
Even though these reactions are hypothetical, an agreement exists in the literature on the importance of hydrocarbons in plasma chemistry. It is believed that hydrocarbons play the following important functions in NTP:[197]

- HC lower the electrical energy requirement for oxidation of NO to NO_2

- HC minimize the formation of acid products

- HC suppress the oxidation of SO_2 to SO_3

Since very few exhaust gas components are unaffected by the NTP, plasma devices were being developed to target a number of pollutants. Some of these approaches turned out to be either impossible or to require excessively high energy densities, others still show promise and are under continuing development, as summarized in Table 2-24.

Table 2-24. Possibilities of pollutants control by plasma.

Process	Development Status
NO Reduction	NO_x reduction by plasma alone is not believed to be a feasible process. Despite years of research, no convincing experimental demonstrations have been shown. Theoretical modelling indicates that NO reduction by plasma would require prohibitively high energy deposition.
NO Oxidation	Oxidation of NO to NO_2 remains the most promising plasma process, which can be realized using realistic energy depositions. The plasma generated NO_2 facilitates NO_x reductions in plasma catalyst systems.
HC Oxidation	Technically possible, but requires high energy rates. Not feasible for diesel, but investigated for cold start HC removal from gasoline engines.
PM Control	NTP can oxidize carbonaceous PM if long residence times are provided, e.g., through particulate "trapping" in the plasma device.

C.7.5. NO Reduction by Plasma

Theoretically, nitric oxide can be chemically reduced through a number of plasma reactions, such as (1) direct NO dissociation followed by the formation of N_2 and O_2 molecules from radicals, or (2) dissociation of nitrogen into atoms, which in turn can react with NO to N_2 and oxygen. Earlier plasma research attempted to maximize this "reduction channel" of plasma over the "oxidation channel" described by reactions (1)-(21). Unfortunately, this task was never achieved and NO reduction by plasma could not be convincingly demonstrated by experiments. A consensus has formed in the current literature that the process is not feasible. This notion is also supported by the following theoretical argument, which estimates the NO_x abatement potential that can be offered by plasma treatment based on energy considerations.

Three minimum energy limits can be considered in regard to the NO reduction by plasma, as follows:

- NO dissociation energy limit

- Nitrogen radical production limit

- Effect of oxygen.

Dissociation energy limit is related to the minimum amount of energy needed to dissociate an NO molecule. In an ideal situation, the kinetic energy of the electrons is dissipated entirely in the dissociation of NO molecules into N and O radicals which would then form exclusively N_2 and O_2 molecules. The energy required to dissociate an NO molecule is 6.5 eV. It can be calculated that this corresponds to the dissociation of 40 ppm of NO per J/L of input energy density. In other words, 10 J/L energy deposition, estimated at about 2 percent fuel economy penalty, would allow to dissociate 400 ppm of NO.

In reality the concentration of NO is very low and direct dissociation of NO is not probable. The kinetic energy of the electrons is deposited primarily into the major exhaust gas components, N_2 and O_2. The electrons could also lose considerable energy through other reactions, such as vibrational excitation of N_2, which do not promote dissociation of NO.

Radical production energy limit can be estimated by assuming the more realistic reaction path through the formation of N and O radicals. The following equations represent the dissociation of nitrogen and oxygen by plasma:

$$e + N_2 \rightarrow e + N(^4S) + N(^4S) \qquad (22)$$

$$e + N_2 \rightarrow e + N(^4S) + N(^2D) \qquad (23)$$

$$e + O_2 \rightarrow e + O(^3P) + O(^3P) \qquad (24)$$

$$e + O_2 \rightarrow e + O(^3P) + O(^1D) \qquad (25)$$
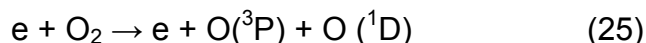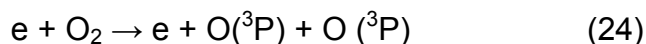
where $N(^4S)$ and $N(^2D)$ are ground-state and metastable exited-state nitrogen atoms, respectively, and $O(^3P)$ and $O(^1D)$ are ground-state and excited-state oxygen atoms, respectively.

$N(^4S)$ is the only plasma species that can chemically reduce NO. Assuming that it is the only radical produced in the system, i.e., reactions (23) - (25) do not occur. Furthermore, assuming that all nitrogen atoms can be used entirely for the reduction of NO according to the following reaction:

$$N + NO \rightarrow N_2 + O \qquad (26)$$

In this case the energy required to reduce NO is simply determined as the energy required to produce N from the electron-impact dissociation of N_2. The number of N_2 dissociations per unit of input energy increases with the electron mean energy. Because of the electrical breakdown threshold, the electron mean energy in non-thermal plasma reactors is around 4 eV. Assuming that the electrical breakdown limit is increased to a very high value of 10 eV. It can be calculated that for a 10 eV electron mean energy about 1.25 N_2 molecules dissociate for each 100 eV of input energy. This translates to the consumption of 40 eV of electrical energy per each N atom produced. This is the minimum energy required under the most ideal plasma conditions to produce 1 atom of nitrogen and, according to reaction (26), to reduce 1 molecule of NO. It can be further calculated that this corresponds to the reduction of 6.5 ppm of NO per J/L of input electrical energy density. This time a 10 J/L input energy deposition (2 percent fuel economy penalty) results in the reduction of only 65 ppm of NO. Reducing NO levels of 650 ppm, as may be seen in heavy-duty diesel engines, would require a prohibitive input energy deposition of 100 J/L.

Effect of oxygen, although difficult to estimate in numbers, will further increase the above minimum energy requirement for NO reduction. This is caused by at least three reasons:

1) The dissociation energy of O_2 is smaller than that of N_2 resulting in a significant fraction of the input electrical power being dissipated in the dissociation of O_2 to produce oxidative radicals (reactions (24) and (25)). The generated ground state oxygen atoms will oxidize NO to NO_2.

2) The metastable nitrogen atoms, $N(^2D)$, react preferentially with oxygen to produce NO. If the electron mean energy is increased to favor dissociation of N_2 rather than O_2, even more excited state nitrogen atoms are generated.

3) The metastable oxygen atoms, $O(^1D)$, react with H_2O to produce OH radicals which in turn react with NO and NO_2 converting them to nitrous acid and nitric acid, respectively.

In the light of the high minimum energy limit for NO reduction it is not believed that plasma treatment alone, in the absence of heterogeneous reactions, may become an effective means of exhaust NO_x abatement. Rather, plasma has to be combined with other technologies, such as emission control catalysts.

C.7.6. NO Oxidation

Plasma was found to be effective in selective oxidation of NO to NO_2. Although this reaction does not bring any emission benefit in itself, the generated NO_2 is a very reactive species, which can be utilized for selective NO_x reduction in plasma catalyst systems or for PM oxidation in plasma devices.

The presence of hydrocarbons is critical to the NO/NO_2 shift in plasma, especially at higher temperatures, such as those encountered in exhaust gases. The optimum HC_1/NO_x ratio is believed to be about 6.[199] At this ratio, the energy density to achieve maximum oxidation efficiency at high NO concentration (600 ppm) is below 30 J/L. At lower NO concentrations (100 ppm), the maximum oxidation efficiency can be achieved at energy deposition of only 6 J/L. An example relationship between the energy density and the NO/NO_2 shift for two initial NO concentrations is shown in Figure 2-102. The lines denote modeling predictions, the points represent experimental measurements.
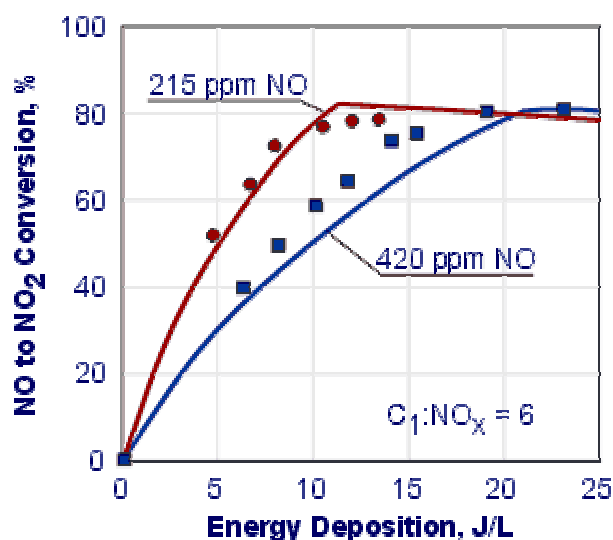
Figure 2-102. Oxidation of NO to NO_2 by plasma.
(10% O_2, 10% CO_2, 5% H_2O, balance N_2; propene additive; t = 200°C).

The HC_1/NO_x ratio of 6 is much higher than that in the native diesel exhaust, which is always below 1. Therefore, the use of plasma induced NO/NO_2 shift is likely to require some enrichment of the exhaust gas with hydrocarbons (e.g., using diesel fuel) at an additional fuel economy penalty.

C.7.7. HC Oxidation

As shown earlier, the chemistry of HC oxidation and the chemistry of NO oxidation in plasma are strongly coupled. However, much higher energy deposition is required to completely oxidize hydrocarbons to CO_2 and H_2O. At energy densities required for the NO oxidation, the post reaction mixture contains such products of partial HC oxidation as aldehydes, ketones, organic acids, and CO. For example, it is possible to convert 100 ppm of NO to NO_2 with less than 10 J/L, but complete oxidation of the resulting 50 ppm of formaldehyde requires more than 150 J/L.[199] Therefore, in view of such more effective technologies as the diesel oxidation catalyst, plasma cannot be considered an attractive option for the abatement of diesel HC. However, plasma can be effective at lower temperatures than those required by catalyst. From this reason, plasma is still and option for cold start HC oxidation in gasoline engines.[200]

C.8. Plasma Catalysts

DeNOx Catalyst: Non-thermal plasma can be used to enhance the performance of deNOx (lean NO_x) catalysts promoting selective catalytic reduction of NO_x by hydrocarbons. There are two possible configurations of the plasma catalyst system:

1) Single stage reactor, usually in the form of the packed bed NTP reactor, where the catalyst is present in the plasma reactor bed.

2) Two-stage reactor, with a monolithic catalyst positioned downstream of the NTP reactor. This configuration, utilizing various types of the parallel plate DBD plasma reactor, appears to be preferred in more recent research.

Experimental work was conducted in a small laboratory packed bed plasma reactor that was filled with different dielectric packings. Simulated exhaust gas containing 7.5% O_2, 4% CO_2, 2% H_2O, 0.2% CO, 750ppm C_3H_6, and 270 ppm NO was used. The space velocity in the reactor was approximately 7,500 1/h. Investigated packing materials included zirconia, barium titanate, and various types of zeolites. Experiments were conducted at the bed temperature of 100, 140, and 180°C. Zeolite material was investigated in a fresh and sintered state. Concentrations of NO and NO_x were measured at the reactor inlet and outlet. The decrease of NO was always higher than the decrease of NO_x, indicating that NO was partially oxidized to NO_2. Results presented as normalized concentration profiles for NO and NO_x as a function of the input energy density, are shown in Figure 2-103.

The solid lines represent material sintered at 800°C with little surface area left. The dashed lines represent fresh zeolite. The "fraction reduced" lines indicate the ratio of NO_x concentration change to the NO concentration change. A similar decrease of NO is observed in both cases while the NO_x performance is dramatically altered in the sintering process. The

fresh zeolite reduces about 50 percent of the total NO$_x$ at high energy densities. The sintered material is capable of reducing only about 20 percent of NO$_x$.
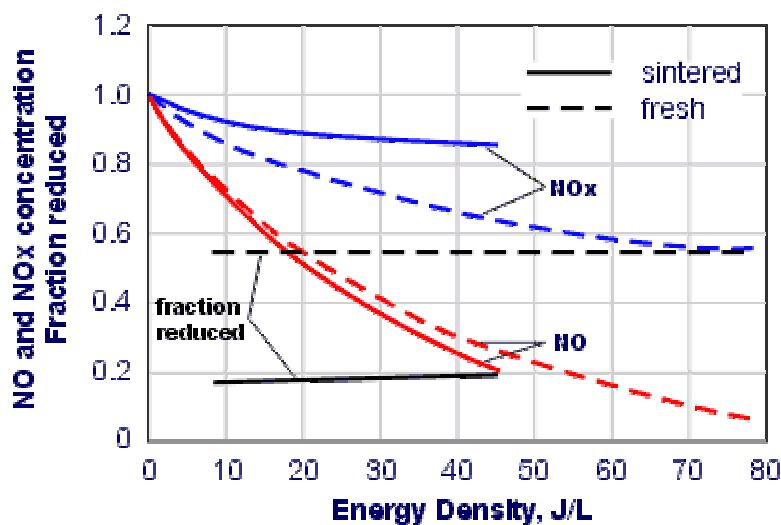
Figure 2- 103. NO$_X$ performance of fresh and sintered zeolite.

Additional experiments showed that the catalyst performance was also improved by increasing oxygen and propene concentrations. Added oxygen, as well as added propene, improved the energy efficiency, i.e., NO$_x$ conversions occurred at lower energy densities. Increasing oxygen or propene concentrations, however, did not have any effect on the fractions of NO which were oxidized and reduced. This performance is similar to the behavior of zeolite based lean NO$_x$ catalysts that have been reported to improve performance with increasing concentrations of oxygen and hydrocarbons.

A number of later studies, including experiments in the two-stage NTP-catalyst configuration, generally confirmed the above findings. It can be concluded that NO in the plasma catalyst undergoes a two-step reaction process, as follows:[201]

     1) ***Oxidation of NO to NO$_2$ by plasma in the presence of hydrocarbons***. The products include NO$_2$, as well as partially oxidized HC, which may be also enhancing the catalyst performance.

     2) ***Selective catalytic reduction of NO$_2$ to N$_2$ using hydrocarbons***. It is suggested that NO$_2$ is the main species that reacts with HC on the catalyst sites, in a process similar to that in the deNOx catalyst. However, even though the importance of the NO$_2$ intermediate appears to be confirmed in the literature, the exact mechanisms remain unclear and may be more complicated than a simple selective reduction by hydrocarbons.[192,200] Catalyst formulation has significant influence on the performance in this second step.

Many catalyst systems have been tested in conjunction with plasma, from noble metal catalysts, through various base metal formulations, to a simple δ-alumina catalyst. Best performance has been reported with some proprietary, non-precious metal zeolite formulations. Interestingly, the copper-substituted ZSM5 catalyst (Cu-ZSM5), so effective as

a deNOx catalyst, was found to reduce the NO_2 back to NO, with no useful overall NO_x conversion.

The experience with plasma catalyst systems can be summarized as follows:

- Plasma catalysts can achieve about 50-60 percent NO_x reductions at an overall fuel economy penalty (electrical + secondary HC injection) of about 5 percent. In this respect, plasma catalyst and active deNOx catalysts offer similar performance, as illustrated in Figure 2-104.[203]
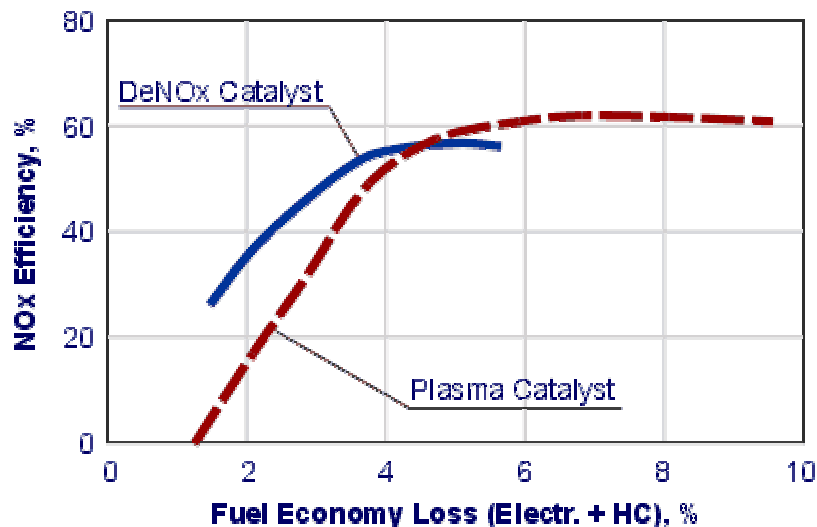
Figure 2-104. Modeled performance of plasma and Denox catalysts.
(2.5 liter TDI engine, 5 liter catalysts, projected FTP-75 cycle, plasma: 5.5:1 HC$_1$:NO$_x$ ratio, DeNOx: varying HC:NO$_x$ ratio).

- Zeolite catalysts used in plasma systems convert about 80% of NO_x to N_2, and 20% to N_2O.

- Plasma catalysts oxidize only about 5% of exhaust SO_2 to SO_3, resulting in no sulfate particulate formation.

- Hydrocarbons, aldehydes, and CO generated by plasma are not affected over the catalyst. An oxidation catalyst is required downstream of the plasma catalyst.

- To achieve significant NO_x conversions, plasma catalysts have to be operated with electrical energy deposition of at least 15 J/L, an HC:NO_x ratio of at least 5, and at low space velocities of 5,000 - 10,000 1/hr.

- Plasma catalysts can provide significant NO_x conversions at temperatures as low as 100°C.

C.9. SCR (Urea) Catalyst

Plasma has been also studied in combination with selective catalytic reduction (SCR) of NO_x using ammonia and/or urea.[204] The objective is to improve the cold start NO_x performance of SCR systems for diesel cars. It is known that the performance of SCR catalysts can be enhanced by increasing their inlet NO_2 concentration. Therefore, oxidation catalysts have been placed in front SCR catalysts to oxidize NO. Replacing the oxidation catalyst with plasma is expected to enable higher NO_x reductions at low temperatures.

Preliminary reports indicate that the low temperature SCR catalyst efficiency can be significantly improved by plasma.[205] The estimated energy costs are lower in comparison to the cost of heating the oxidation catalyst. Potential problems in the application of plasma to SCR are related to the formation of ammonium nitrate aerosols, which would increase PM emission.

C.10. Particulate Matter Control by Plasma

PM Oxidation by Plasma: In comparison to the wealth of publications on NO_x control by plasma, little research has been done on the application of NTP for the control of diesel particulate emissions. For some time it was not obvious whether plasma devices can have an effect on PM emissions at all. Research studies carried out in the late 1990's indicate that diesel particulates can be oxidized, and PM trapping devices can be regenerated, using NTP. More precisely, the diesel particulates can be effectively oxidized by some reactive species generated in plasma, such as O and OH radicals or NO_2. An important advantage of plasma is the potential to oxidize particulates at low exhaust temperatures.

Diesel PM, when measured on the molecular scale, is characterized by large particle sizes. For this reason, the oxidation of particulates by plasma is possible only if the PM residence time in the reactor is much longer than the residence time normally required for gaseous species. In other words, in a typical plasma reactor, gas-phase oxidation of PM would be incomplete at energies suitable for the control of gas-phase species.[199] This observation is not surprising; in fact a similar residence time argument is made to explain why carbonaceous PM can be catalytically oxidized in a diesel particulate filter but not in a diesel flow-through catalyst. In order to increase the residence time without increasing the reactor size beyond reasonable limits, the particulate has to be removed from the gas stream (trapped) and held in the reactor until its oxidation is completed. Two reactor configurations have been proposed to achieve this objective in a plasma device:

- Single-stage reactor, where a packed bed plasma reactor acts as the PM trapping device, and

- Two-stage reactor, where a "classic" diesel particulate filter (DPF) is positioned downstream of the plasma generator.

The role of plasma in the two-stage configuration is to generate NO_2 and, possibly, ozone that can oxidize particulates in the downstream filter. Plasma chemistry in this case is similar to what was seen in the reactors designed for NO_x reduction.

The chemistry in the single-stage plasma PM-reducing device, however, appears to be quite different. The presence of carbonaceous particulates in the reactor influences plasma reactions. When particulates are present, less hydrocarbon oxidation is observed and less NO_2 is generated. Furthermore, PM reductions can be achieved at $HC_1:NO_x < 1$, a mode where NO_2 production is not very efficient. Although the reaction mechanisms are not understood, it is speculated that particulates can be oxidized by different plasma species than NO_2, presumably by O and OH radicals.[196]

C.11. Single-Stage Packed Bed Plasma Reactor

In the packed bed configuration, the PM is trapped in the NTP reactor itself. NTP packed bed reactor packings, in the form of beads or pellets typically made of such ferroelectric materials as barium titanate, magnesium niobate, lead titanate, or lead zirconate, can be designed to trap particulates, primarily through electrostatic impaction. In addition, a separate pair of electrodes may be provided upstream of the reactor to increase the trapping efficiency by electrically charging soot particles entering the reactor.[206]

One of the early reports on the use of a packed bed plasma device for PM control (Figure 2-105) was published by SwRI in 1995.[207] The tests were conducted with a 2.2 liter Toyota diesel engine on a chassis dynamometer at 60 mph and 13.1 hp road load. A partial exhaust gas flow set-up and a small packed bed plasma reactor utilizing a barium titanate type of ceramic material were used.
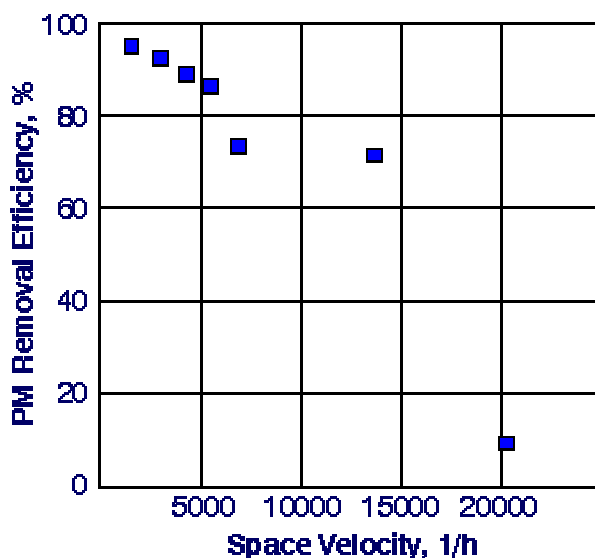
Figure 2- 105. Particulate matter removal efficiency by plasma.

Very high PM removal efficiencies which were observed at low space velocities would suggest that both the SOF and the elemental carbon fractions of diesel particulates were affected by plasma. An accompanying NO_x removal was also recorded during the tests. The authors estimated that the power consumption of 1.1 kW would be needed by a system capable of handling the entire exhaust gas flow from the 2.2 liter Toyota engine.

A full-scale prototype of a plasma PM removal device for a diesel car was developed by AEA Technology.[196] The system, shown in Figure 2-106, utilizes a bed of ceramic pellets placed between two cylindrical electrodes. Perforation and a system of channels in the inner electrode direct the exhaust gas flow through the pellet bed. The reactor has an active volume of 2600 cm^3 and replaces the original muffler on the test vehicle - a 1994 MY LTI Fairway London Taxi equipped with a Nissan 2.7 liter IDI diesel engine.
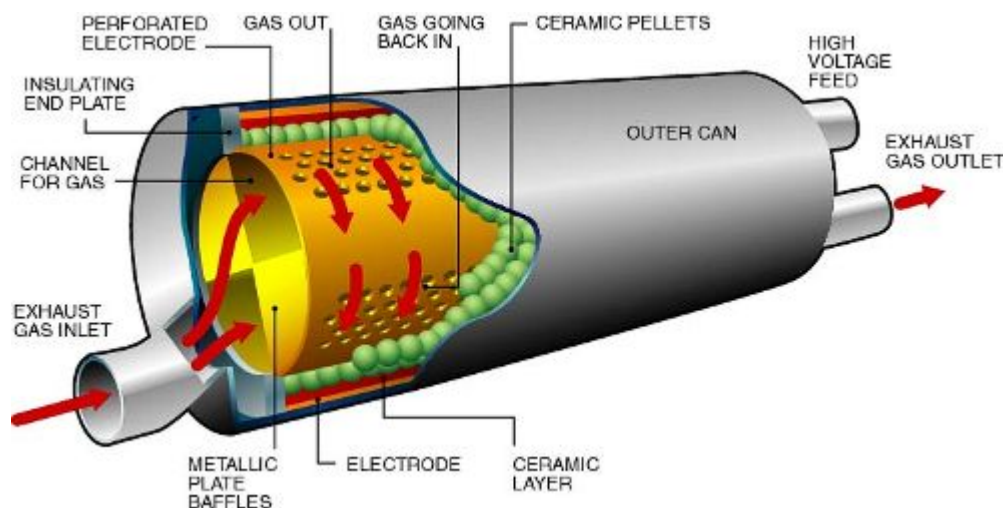
Figure 2-106. Plasma device for diesel particulate removal.
(Courtesy of AEA Technology).

The unit was reported to support low temperature, complete oxidation of soot during vehicle tests. No blow-through of PM was observed, even after long periods of operation. There was no particle build-up on the packing material, which remained relatively clean during plasma experiments. Vehicle tests were performed with no hydrocarbon enrichment of the exhaust gas.

Emission measurements over the ECE+EUDC test yielded about 50 percent PM emission reduction at ambient temperature of 25°C and about 70 percent reduction at 0°C. It was speculated that these results could be increased by optimizing the reactor packing material for higher trapping efficiency. The device provided a 90 percent conversion efficiency (and a 99.9 percent steady-state efficiency) for ultrafine particulates of 60 nm diameter. High removals of PAHs was also measured in the plasma device.

The authors determined the upper energy limit required for the NTP low temperature oxidation of PM at 0.34 kWh/g. This number was calculated from steady-state experiments running 2.34 g/h of PM that was completely oxidized at an input energy deposition of 18 J/L.

C.12. Two Stage Reactor: NTP - DPF Configuration

The two-stage reactor configuration, Figure 2-107, corresponds to the CRT filter layout, where NO_2 is generated by plasma, rather than over an oxidation catalyst. The plasma generated NO_2 facilitates low temperature regeneration of the particulate filter.[208] In this

configuration, plasma-generated ozone may also play a role in the filter regeneration. Ozone was reported to be particularly effective at causing low temperature combustion of soot accumulated in diesel filters.[209]
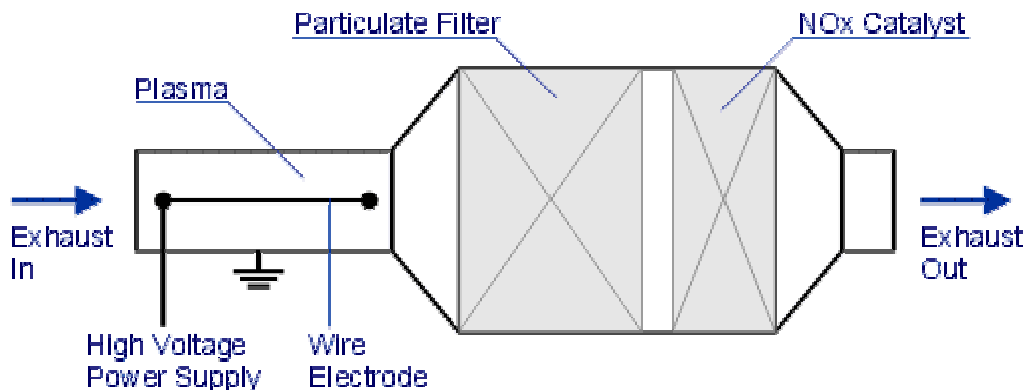
Figure 2-107. Plasma regenerated particulate filter system concept.

The system presented in Figure 2-107 includes a NO_x reduction catalyst downstream of the filter. This diagram is an example of wishful thinking about simultaneous reduction of NO_x and PM emissions by plasma. In reality it is not yet clear if such system is feasible. As already mentioned, it is believed that the generation of NO_2, which is essential for catalytic NO_x reduction, is impaired by particulates due to the competition between NO and carbon for the oxygen radicals in plasma. As an alternative approach, it was suggested that the simultaneous NO_x and PM control could be realized by designing the plasma catalyst reactor for maximum NO_x reduction and periodically switching into the thermal (hot) plasma operation mode in order to thermally oxidize particulates.[199]

C.13. Future Issues

Plasma studies are being conducted by a number of government and private sector organizations in the US and in Europe. The major areas that need further research or require improvement can be grouped as follows:

1) Improvement in the NTP reactor design with possible savings in electrical energy consumption; control of electromagnetic interferences required for commercial applications.

2) Understanding of the reaction mechanisms in plasma, in plasma catalysts, and reactions in the presence of diesel particulates.

3) Increasing the NO_x conversion efficiency and decreasing the catalyst size (i.e., increasing the space velocity).

4) Refining PM removal reactors and increasing the removal efficiencies.

5) Studying the possibilities of simultaneous NO_x and PM removal.

3.0 EMISSION REDUCTION TECHNOLOGY VERIFICATION

In this section, an overview is provided of the technologies reviewed in Section 2 in terms of the level of maturity for each technology. Technology maturity includes the practical feasibility, level of commercialization, and the official status of verification by EPA or by California's Air Resource Board (ARB). A summary of each technology's emission reduction potential, technical feasibility (level of demonstrated emission reductions on field equipment), verification status (as of January 2003), and other comments is provided in Table 3-1 with further explanation below.

Table 3-1. Emission reduction technologies emission reduction potential, level of feasibility, and verification status.

Technology	NOx Reduction Potential (Accepted or Vendor Claim)	Feasibility	Verification Status	Comment
Fuel Measures				
Fuel reformulation (e.g. cetane enhancers)	Up to 5% (Beyond Texas low emissions diesel (LED)	High	EPA Model	
Fischer-Tropsch	Up to 14 % (Beyond Texas LED)	High	EPA Model	Undergoing further tests
Fuel-water emulsion	14% - 16% (ARB) ~13% Hwy (in 2007) ~20% Nonroad (in 2007)	High	Verified	California certified EPA special report
New Engine, Vehicle, or Repower				
Clean Diesel	Up to 80% Highway Up to 50% Nonroad	High	Certified engines	Replacement engines/fleet modernization; Most widely used in TERP
CNG\LNG	Typically more than Clean Diesel options	High	Certified engines	Replacement engine or retrofit kit
Hybrid System	Up to 40% in absence of clean engines	Medium	Certified engines	Several demonstration + Energy Savings; TCET funded demonstration
Engine Retrofit or Aftertreatment				
Water Injection	Up to 50% reported	Low	Not verified	Demonstrated on marine engines
Humidified Air	Up to 50% reported	Low	Not verified	Demonstrated on marine engines
Injection retard (with PM Control)	~ 25%	High	ARB verified	Needs low sulfur fuel
Turbocharger (with aftercooling	NA	Low	Not verified	Maybe only applicable to precontrolled engines
Intake manifold and port designs	NA	Low	Not verified	Maybe only applicable to precontrolled engines
Combustion chamber design	NA	Low	Not verified	Maybe only applicable to precontrolled engines
Fuel-injection systems	NA	Low	Not verified	Maybe only applicable to precontrolled engines
Exhaust gas recirculation (EGR)	Up to 50%	Medium	Uncertain	TERP funded project
Lean NOx catalyst	20 – 35%	High	Durability testing ongoing in California	TCET funded verification program
NOx adsorber	Up to 90%	Low	Not verified	In development (Needs low sulfur fuel)
Selective Catalytic Reduction (SCR)	Up to 90%	Medium	EPA evaluation process	TERP funded project (Does not need low sulfur fuel)
Plasma Reduction	Up to 90%	Low	Not verified	In development

Additional emission reduction technologies that might be considered under the advanced technology eligibility criteria are shown in Table 3-2. In each case, it might be necessary for Texas State officials to determine whether each type of technology is eligible for TERP funding under the current guidance. However, TCET could provide a role in accelerating the use of these technologies through targeted assistance and funding demonstration projects.

Table 3-2. Other technology options.

Technology	NOx Reduction Potential	Feasibility	Verification Status	Comment
Turbine engines	Up to 90% (50% cleaner than best current diesel)	High	California Certification with diesel *	Fuel types; diesel, LPG, or CNG. Steady-state or hybrid operation applicability.
Electrification	100%	High	No need	Straight-forward impact
Fuel Cells or Solar Cells	Up to 100%	High	Demonstration projects	Application limited to semi-stationary equipment types
Spark-ignition with 3-way catalyst	~ 90%	High	Certified engines	Uncertain whether applicable under TERP

* - Certification information for a hybrid-electric bus at http://www.arb.ca.gov/msprog/moyer/certeng.htm

In this review of TERP eligible control measures, one goal was a 'needs' assessment and interpreted here as one or more of the following; additional technology development, barriers to commercialization, verification assistance, or reducing the cost of implementation. Discussed below is the verification process that needs to be completed before EPA would accept the emission reductions as applicable to SIPs, and an assessment of the verification status, commercialization by vendors, and engineering applicability.

3.1 VERIFICATION PROCEDURE

The verification procedure for demonstrating emission reduction technologies is described in a series of EPA publications[1,2] and from ARB[3]. The EPA process would likely be considered the only applicable process, however because ARB-approved retrofits emission reduction would be incorporated into EPA-approved California State Implementation Plans, ARB approved retrofits would have tacit approval from EPA.

The EPA verification process is outlined at http://www.epa.gov/otaq/retrofit/documents/flowchrt.gif and involves a multistep process with personnel from the Environmental Technology Verification (ETV) and cooperating staff from EPA's Office of Transportation and Air Quality (OTAQ).

- Initial Verification
  - Initial Contact
  - Submission of intent to verify form and background information
  - Assign OTAQ contact
- Pre-Verification
  - Submit application
    - Test plan
    - Initial verification vs. product upgrade
- If verification needed, then begin official test plan

- o Emission testing protocols
  - Add-on retrofit or engine upgrade or
  - Fuel and fuel additives
  - Selective Catalytic Reduction technology
- Assess test data
  - o Complete application package?
  - o Applicable to which engine families?
  - o Determine emission reduction
  - o Evaluate operating criteria
  - o Assess in-use data

After this process, ETV may request additional in-use testing if the laboratory testing is not considered sufficient. OTAQ may compare test results with those of other testing programs especially for fuel reformulations including biodiesel and fuel/water emulsions.
The verification process entails laboratory trials to verify the effectiveness and subsequent in-use testing to justify the retrofit durability, especially for catalyst aftertreatment.

In a few cases, EPA deemed it necessary to conduct its own analysis for the emission effects from the use of the Lubrizol PuriNOx process (a fuel/water emulsions) (EPA[4]) and biodiesel (http://www.epa.gov/otaq/models/biodsl.htm) though biodiesel does not provide NOx emission reductions. EPA also has a separate ongoing process to evaluate other fuel reformulations (http://www.epa.gov/otaq/models/analysis.htm) and Selective Catalytic Reduction (SCR) retrofits.

The current retrofit technologies that have been verified have been limited to devices intended to control particulate matter (PM). Table 3-3 shows the retrofit technologies that have been approved by EPA as retrofits for diesel engines, which only address HC, CO, and PM emission reduction methods.

Table 3-3. EPA verified emission reduction technologies.

Verified Retrofit Technologies					
Mfr	**Technology**	**PM%**	**CO%**	**NOx%**	**HC%**
Engelhard	DPX Catalyzed Diesel Particulate Filter	60	60	n/a	60
Engelhard	CMX Catalyst Muffler (2 cycle engines)	20	40	n/a	50
Engelhard	CMX Catalyst Muffler (4 cycle engines)	20	40	n/a	50
Engine Control Systems	AZ Purimuffler (2 cycle engines)	20	40	n/a	50
Engine Control Systems	AZ Purimuffler (4 cycle engines)	20	40	n/a	50
Johnson Matthey	Continuously Regenerating Technology (CRT) Particulate Filter	60	60	n/a	60
Johnson Matthey	CEM Catalyst Muffler (2 cycle engines)	20	40	n/a	50

ARB[5] has a similar but separate verification process, which has yet to be finalized but the suggested process is outlined below.

- Submit Testing Protocol
  - o ARB review and approved or revised (up to 30 days minimum)

- Testing
  - Laboratory
  - Field
  - Durability
  - Other
- Submit application
  - ARB review (up to 60 days minimum)
  - Further testing if needed
  - Or, Executive Order approval

ARB has also separately verified certain fuel programs including PuriNOx and Aquazole, both fuel/water emulsions. (http://www.arb.ca.gov/fuels/diesel/diesel.htm)

ARB has verified only one NOx control strategy, Cleaire's "Flash and Catch" (for on-road Cummins M11 engines only) reducing NOx by 25% with addition reductions in PM emissions. This strategy combines a recalibration of the injection map (retarded timing) to lower NOx emissions but increases PM combined with a particulate filter to eliminate any PM increases.

In summary the verification procedure can be costly and applicability limited to a few engine model or families. Regulators, EPA and ARB, are balancing the desire to simplify and lower the cost of the process while ensuring that verified technologies reduce in-use emissions. However, vendors who assume the burden and risk of developing technology and the verification will see cost of implementation rise. Also, vendors may have difficulty applying their technology widely, having to verify the device on each engine family. The result has been to reduce the number and variety of emission control measures available.

TERP has funded more technology options than have been given verification status. While the technology has been developed, the verification status lags for TERP-funded projects involving EGR retrofit kits, SCR add-on devices, and TCET-funded projects for lean NOx catalysts and emission reduction credits for diesel-electric hybrid systems. This funding may lead to increasing the number of verified technology options for future projects. TERP also has had a requirement that retrofit devices or repowered engines provide more than a 30% NOx reduction limiting the number of retrofit options.

3.2 FUEL MEASURES

There are three fuel options that have been shown to have potential to reduce NOx emissions from diesel engines including fuel additives to improve cetane levels, reformulating the fuel for lower aromatics and higher natural cetane levels (as characterized in the extreme by Fischer-Tropsch derived fuels), and fuel/water emulsions.

EPA[6] has issued a paper reviewing the emission effects of fuel reformulation including the effect of cetane improving additives. For cetane improvers (typically 2-ethylhexyl nitrate or d-t-butyl peroxide or other peroxides and ethers), EPA predicted that an additive that improved the cetane number by 5 points would result in a 1.4% NOx reduction for on-road engines and a 2.1% NOx reduction with off-road engines in 2007. It could be possible to add sufficient

cetane additive to improve cetane levels by 10 points or more, but EPA found diminishing emission benefits with higher levels of cetane levels.

Besides cetane improvers, Mason and Buckingham[7] found that diesel NOx emissions were affected by a number of fuel properties including cetane number, amount of cetane improver (discussed above), distillation properties, specific gravity, aromatics level, sulfur and oxygen level. The statistical model that Mason and Buckingham developed could be used to estimate the performance of additional reformulation. For diesel fuel reformulation, the best possible low emission diesel fuel reformulation is likely a fuel made from the Fischer-Tropsch process, which results in a fuel with very low aromatic and sulfur levels, low specific gravity, and very high cetane level. Clark et al.[8] performed a direct emission comparison between the Fischer-Tropsch fuel and the California reformulated diesel (Texas Low Emission Diesel is expected to have the same emission performance as the California reformulated diesel) finding a NOx emission reduction of 12% from California diesel fuel.

EPA[9] performed an analysis of the test data for Lubrizol's PuriNOx product and estimated emission improvements with its use. EPA found the percent NOx emission benefit from the use of PuriNOx was proportional to base emissions level, so lower benefits were projected for the use of PuriNOx for on-road vehicles (13% in 2007) than for off-road engines (20% in 2007) where on-road vehicle/engine meet lower emission standards. Also, as the fleets of engines turnover, the benefit of PuriNOx is expected decrease in subsequent years. The emission benefits verified by ARB[10] for two fuel/water emulsions (PuriNOx and Aquazole) were 14 and 16% similar to that projected by EPA.

3.3 ENGINE REPOWER OR NEW ENGINE/VEHICLE/EQUIPMENT PURCHASES

Many of the TERP funded projects (TCEQ, [11]) consist of purchase of cleaner new engines or vehicles or off-road equipment and scrapping serviceable but high emitting engines. This type of emission reduction strategy is similar to that primarily used in the California Carl Moyer program (http://www.arb.ca.gov/msprog/moyer/moyer.htm) and Sacramento's SECAT program (http://www.4secat.com/index1.html). It consists of replacing the engine or the entire on-road vehicle or off-road equipment with a new lower emitting engine and scrapping the current vehicle prior to the end of its useful life.

With this initiative a new engine certified to a lower emission level than the current engine is installed or 'repowered' into the new equipment. The emissions difference can be calculated using the difference in certification emission levels between those modeled for the current equipment (the current engine may either not have been certified or modeled to not meet its emission standard). The engine repower can be either with a cleaner diesel or alternatively-fueled (primarily compressed or liquefied natural gas) engine or in some cases converted to a CNG/LNG engine meeting a lower emission standard.

By purchasing a new engine or vehicle there exists the opportunity to improve emissions rates beyond the average emissions of all new engine/vehicles. Lower emitting engines could be purchased or the vehicle could be redesigned to be more efficient. Replacing the engine or vehicle is the most straightforward emission reduction technology because it does not require separate verification approval for its use beyond the initial emission certification.

For on-road vehicles, hybrid electric designs can be used to recover lost energy during braking events and improve the overall emission performance of a vehicle in-use. NAVC[12] reviewed data on hybrid vehicle designs and concluded that these vehicle designs could improve fuel economy and NOx emissions by 25% without using cleaner technology engines.

3.4 ENGINE RETROFIT

There are several retrofit initiatives that are being actively marketed or demonstrated with field testing in Texas and California. These include injection timing reprogramming with particulate traps (such as Cleaire's "Flash and Catch"), exhaust gas recirculation (EGR) systems with particulate traps (such as STT Emtech http://www.sttemtec.com/), lean NOx catalysts (such as marketed by Cleaire "Longview" system), and selective catalytic reduction (many vendors of SCR systems). Other engine retrofit options listed in Table 3-1, such as the burgeoning technologies of NOx adsorbers or plasma NOx reduction methods, require additional development work prior to performing demonstration projects.

Injection timing modifications can be used to reduce NOx emissions, but the most applicable type of modification, retarded timing, results in higher PM emissions. Therefore the only verified method of injection timing modification of in-use engines requires the addition of a particulate trap. A PM trap requires low sulfur fuel (<15 ppm) to function properly. In addition implementation of this approach may reduce fuel economy. The 30% control minimum require of TERP may limit the use of this technology.

EGR is a technology being implemented for some heavy-duty on-road truck engines now sold. Either as a new technology or as a retrofit, the concern with EGR is recycling exhaust pollutants into the engine, so a particulate trap and low sulfur fuel would likely be needed to be effective as a retrofit strategy. TERP provided funding for a large project involving EGR retrofits, which would likely include emission reduction verification.

Lean NOx catalysts are aftertreatment catalysts that have been developed to reduce NOx emissions under lean conditions found with diesel engines. One advantage of these systems is that they could be widely applied to existing engines. The main concern with these systems has been the durability of the catalysts, so ARB verification has been reserved until after furability testing has been completed. TCET has funded of a lean NOx catalyst system that may initiate verification of this technology. The 30% control minimum require of TERP may limit the use of this technology.

Selective catalytic reduction (SCR) has been available for many years for use in stationary sources, but has been slow to be applied to mobile sources. Because mobile sources typically demand transient loads, it is difficult to properly meter the reactant (either urea or ammonia) into the exhaust to prevent large emissions of ammonia. Some successful demonstration of SCR have been applied to marine engines, diesel generators, and other applications typically operated at near steady-state conditions or else require extensive engine mapping (understanding fuel/load/speed) need to be investigated prior to installation of the SCR system. EPA[13] has a special ongoing but not yet completed program for verifying SCR technologies. The advantage of SCR is that a high level of NOx reduction (>90%) is possible and that it does not require low sulfur fuel.

NOx adsorber technology or plasma NOx reduction methods are in rapid development for use in not currently available but are in rapid development for use in meeting the 2007 on-road heavy-duty engine standard. As the date for compliance with this standard draws closer, retrofits with this technology may become available, but is not available at this time.

3.5 ADDITIONAL OPPORTUNITIES

There are additional technology options to provide NOx emission reductions, but it is unclear that these would qualify under the TERP eligibility criteria. In each case, the technologies are being used in field applications.

Turbine engines can run on a variety of fuels including diesel fuel and are in service primarily providing continuous or emergency electric generation capability as a small stationary source. Turbines may also be used instead of diesel engines to provide electric power for hybrid electric vehicles and was certified in California for use in a hybrid electric transit bus. Turbines produce much lower NOx than diesel engines regardless of the fuel used. Turbines work best when operated at a relatively high constant load, so the transient nature of loads required of mobile sources may make it difficult to directly replace diesel engines except in rare situations, such as in a mobile generator.

Replacing a diesel engine with a battery, or fuel or solar cell is a widely accepted measure to reduce emissions. In each case, the engine power would be replaced by an alternative energy source. Battery power would need recharging using grid power but is otherwise a zero emitting source. Fuel cells are being investigated for on-board power or to use as a charging station for battery powered for mobile sources. Solar cells and batteries have been in-use already for some applications such as signal boards, which would otherwise be powered by small diesel engines.

Large spark-ignition (using gasoline, LPG, or CNG fuel) engines may be refitted with three-way catalysts such as are commonly used for light-duty cars and trucks. Heavy-duty on-road trucks and off-road equipment using spark-ignition engines are not currently required to implement three-way catalyst technology, but could be retrofit for this technology. Three-way (reducing three pollutants, VOC, CO, and NOx) catalysts require the engine to be operated stoichiometrically (the combustion mixture is equally balanced between fuel and air), so an engine control system must be installed and coupled with exhaust sensors prior to installation of the three-way catalyst. There could be many vendors of such systems with one of the best known being Engine Control Systems (http://www.lubrizol.com/EngineControl/material_handling/default.htm). Retrofit of spark-ignition engines however are not eligible for TERP funding.

4.0 COSTS AND COST EFFECTIVENESS

The cost effectiveness calculation is important for determining the eligibility of proposed projects. Cost can be viewed in terms of capital amortized over the life of the project combined with continuing operating cost or as a one-year cost effectiveness where the total cost of the project is compared with the emission reductions in the attainment year. The first cost effectiveness method is the official TERP eligibility criteria and is also called an annualized cost effectiveness where projects must not be greater than $13,000 annualized cost per annual NOx ton reduced. The second one-year cost effectiveness calculation is useful for determining the total cost for the air quality goals.

The annualized cost effectiveness can be calculated through the equations shown below. The annualized cost effectiveness method encourages longer-term retrofit or replacement projects through the calculation method where the higher the project life the lower the cost effectiveness value. (As noted below the California Carl Moyer program uses a higher rate of return in its calculation resulting in a 6% higher cost effectiveness for 5 year projects and 10% higher for 10 year projects, so reported Carl Moyer cost effectiveness values were adjusted downward by 6% to compare with the TERP cost effectiveness estimates.)

Capital Recovery Factor (CRF) = [(1 + 0.03)^n (0.03)] / [(1 + 0.03)^n - 1]

> *Where n is the project life*
> *And 0.03 is the annual rate of return*
> *(California Carl Moyer Program uses 0.05 as the rate of return)*

*Annualized Cost = CRF * Incremental Capital Cost + Operating Cost*

Annualized Cost Effectiveness = Annualized Cost / Annual Emission Reduction

Another method is to determine a 1-year Cost Effectiveness making it easier to estimate the budget needed to implement the control measure. This cost effectiveness calculation allows air quality planners to quickly estimate the total emission reduction possible in the attainment year for a fixed cost and adjust funding levels accordingly. For instance, a 1-year cost effectiveness estimate of $19,000 per annual ton (the Carl Moyer average shown in Table 4-1) provides planners an easy method to estimate the total cost of an air quality goal such as $6.9 million per daily ton of NOx reduced (365 multiplied by $19,000).

1-Year Cost Effectiveness = Project Cost / Emission Reduction in Attainment Year

where Project Cost = Capital cost + operating cost over life of control measure

Typically, most projects request from the TERP or Carl Moyer Programs only the incremental capital cost other than fuel projects where the incremental cost is the fuel. Some projects (especially those using particulate traps) require the use of low sulfur fuel and so may request additional funding to cover the added cost of this fuel. Operating costs are either absorbed by the owner/operator or are requested as an up front sum. Operating costs could be estimated

for the life of the project using the same present value assumptions in the calculation of the TERP cost effectiveness and one-year cost effectiveness described above.

ENVIRON (2003) has prepared on-line tools for determining cost effectiveness and emission reductions from a wide variety of on-road and off-road equipment. These tools are consistent with the use of MOBILE6 for on-road heavy-duty and NONROAD (June, 2000 release) for off-road equipment and use the TERP cost effectiveness calculation method described above. The on-road tool was designed for the Houston-Galveston Area Council to determine the most effect projects to be funded with Congestion Mitigation and Air Quality (CMAQ) funds for the Voluntary Mobile Source Emission Reduction Program (VMEP). The off-road tool was designed for TCEQ (but does not have official TCEQ approval). Cost effectiveness estimates provided in Table 4-1 not otherwise referenced were estimated using these cost effectiveness tools.

Project costing was taken from a number of sources and can have a wide range due to the source and assumptions used in those reports. For instance, funding levels for TERP or Carl Moyer projects may be higher due to the novelty of these types of projects and/or include the costs of obtaining verification in addition to the hardware costs. Also, vendor estimates provided here might be lower than contract prices to cover contingencies associated with the requirements of TERP.

Annotated summary data is provided in Table 4-1 outlining the cost and cost effectiveness of various control measures. Individual projects may have higher or lower cost effectiveness depending upon how much operating costs are included in the project, the project life, emissions level of the equipment prior to implementation of the control measure, and the annual activity of the equipment. In cases where the cost effectiveness was calculated, those not specifically referenced, the operating costs were ignored. Cost effectiveness estimates were typically calculated for a best-case on-road vehicle (a model year 2000 transit bus operating $40,000 miles per year) and for a model year 2000 typical off-road equipment type. A project life was assumed to be 5 years unless the control measure only applied to brand new engines (turbines and hybrid vehicles) where 12 years was used. Longer term projects would provide better TERP (annualized) cost effectiveness estimates. Off-road equipment provides a more cost effective emission source to control because base emissions levels are higher, so more emissions are available per engine retrofit. The Carl Moyer program (ARB, 2002) provides evidence of that where off-road projects had cost effectiveness estimates less than half that for on-road projects. The most cost effective programs were those applied to locomotive, marine (especially ferries), and semi-stationary agricultural pumps (not currently eligible for TERP funding) where high base emissions levels and activity levels result in large potential emission reductions and therefore lower cost effectiveness.

ENVIRON

Table 4-1. Emission reduction technologies cost and NOx cost effectiveness estimates.

Technology	Capital Cost	Operating Cost	TERP Cost Effectiveness	1-Year Cost Effectiveness
Fuel Measures				
Fuel reformulation (e.g. cetane enhancers)	None	$0.08/gallon for 5 cetane points[1]	$45,000 on-road $33,000 off-road	$45,000 on-road $33,000 off-road
Fuel reformulation (Fischer-Tropsch)	None	10% higher[2] (e.g. $0.12 per gallon)	$14,000 on-road $10,000 off-road	$14,000 on-road $10,000 off-road
Fuel-water emulsion	None	$0.25/gallon (PuriNOx™)[3]	$9-$12,000[7]	$9-$12,000[7]
New Engine, Vehicle, Repower				
Clean Diesel	Up to $40,000 per engine	No cost	$5,200 on-road[6] $2,500 off-road[6]	$19,000[6] all
CNG\LNG	Same as above not counting infrastructure costs associated with refueling facilities	Likely lower		
Hybrid System	Up to $180,000 as a prototype $150,000 estimated for this work	-25% Fuel Cost	$75,000	$750,000
Engine Retrofit				
Water Injection	$20 to $25/kW[11] ($19,000 for a 1,000 hp engine)	Slight operating and fuel penalty	$1,500 ferry[11]	$4,000 ferry[11]
Humidified Air	$64/kW[8]	Slight operating and fuel penalty	$3,000 ferry[8]	$9,000 ferry[8]
Injection retard (with PM Control)	$13,000[5]	Fuel economy penalty and low sulfur fuel	$12,000 on-road	$56,000 on-road
Turbocharger (with aftercooling	No vendor	No vendor	NA	NA
Intake manifold and port designs	No vendor	No vendor	NA	NA
Combustion chamber design	No vendor	No vendor	NA	NA
Fuel-injection systems	No vendor	No vendor	NA	NA
Exhaust gas recirculation (EGR)	$21,000[7] $15,000[10]	Slight fuel penalty, added maintenance	$4,600[7]	$32,000[7]
Lean NOx catalyst	$5,000-$10,000 for LNC/DPF combo[4]	Slight fuel penalty	$10,000 on-road	$43,000 on-road
NOx adsorber	Prototype only; not on the market	Prototype only	NA	NA
Selective Catalytic Reduction (SCR)	On-road heavy–duty $10,000-$45,000[4] $144 / kW marine[8] $40 - $60 / kW[11]	Maintenance cost $0.005 kW-hr work[11] (~$600/ton)	~$3,000 ferry[8] $12,000[7]	~$7,000 ferry[8] $56,000[7]
Plasma Reduction	Prototype only; not on the market	Prototype only	NA	NA

Technology	Capital Cost	Operating Cost	TERP Cost Effectiveness	1-Year Cost Effectiveness
Other Technology Options				
Turbines	$40,000 - $67,000[9]	Lower maintenance, longer life, but higher fuel use	$10,000	$104,000
Electrification	$12,000 – $55,000[6] offroad	Fuel savings	$1,300 - $5,800[6]	$6,000 - $26,000[6]
Fuel/Solar Cells	Unknown	Fuel savings	Unknown	unknown
SI TWC	$3,000 per engine	Minimal	~$2,000	~$10,000

1. Based on $50/gallon for additive and 1 gallon additive to 640 gallon diesel ratio as described for EnviroMax http://www.maxmalc.com
2. EPA, http://www.epa.gov/otaq/consumer/fuels/altfuels/fischer.pdf
3. ARB, http://www.arb.ca.gov/regact/bus02/appf.doc
4. Cost information available at http://www.epa.gov/otaq/retrofit/documents/meca1.pdf
5. For ARB-certified Cleaire Flash and Catch. Source: John Egan, Cleaire.
6. ARB (2002); Carl Moyer program
7. TCEQ, 2002[223]
8. Farrell et al. (2002)[220]
9. Capstone (http://www.capstone.com) for turbine costs and Caterpillar for equivalently powered off-road diesel engine
10. STT Emtec, http://www.sttemtec.com
11. Wartsila (2002, 2003)[229]

4.1   FUEL PROJECTS

Fuel projects are unique in that the cost effectiveness for cleaner diesel fuel projects is not affected by the life of the project because the cost is an operating cost not a capital cost. Therefore the annualized and one-year cost effectiveness are the same by definition. To determine the cost effectiveness, a typical on-road and off-road situation was used as shown in Table 4-2. Off-road projects have lower cost effectiveness estimates because base emissions levels are higher so the percentage reduction results in greater emission reduction in terms of tons. Using older equipment would result in greater emissions reduction and therefore lower cost effectiveness estimates; but newer equipment would result in lower tonnage reduction and higher cost effectiveness estimates. The percent reductions in Table 4-2 were taken as conservative values for cetane enhancers and Fischer-Tropsch (FT) fuel because they have yet to be individually verified by EPA though EPA reported emission reductions for these fuels. TERP has funded fuel/water emulsion projects with projected cost effectiveness of between $9,000 and $12,000 consistent with the sample calculation for the off-road Aerial Lifts cost effectiveness shown in Table 4-2.

Table 4-2. Sample fuel projects situations for cost effectiveness analysis.

Project	Sample Vehicle\Equipment	Cost (per gallon)	Reduction	Cost Effectiveness ($/ton)
Cetane Enhancer	2000, Transit Bus	$0.08	2%	$45,000
	2000, Diesel Aerial lift, 175 hp	$0.08	2%	$33,000
FT fuel	2000, Transit Bus	$0.12	10%	$14,000
	2000, Diesel Aerial lift, 175 hp	$0.12	10%	$10,000
Fuel/water Emulsion	2000, Transit Bus	$0.25	13%	$22,000
	2000, Diesel Aerial lift, 175 hp	$0.25	20%	$10,000

4.2   NEW ENGINE, VEHICLE, OR REPOWER

The most prevalent project type for TERP, Carl Moyer, and the Sacramento Emergency Clean Air Transportation (SECAT, http://www.4secat.com/index1.html) programs have been replacing existing engines or purchase of clean new vehicles or equipment to replace in-use equipment. The cost effectiveness for engine replacement projects provided in Table 4-1 was taken from Carl Moyer averages, but as shown in Table 4-3 the cost effectiveness of individual projects can vary widely.

Table 4-3. Sample new engine projects situations for cost effectiveness analysis.

Project	Sample Vehicle\Equipment	Cost (per gallon)	New Engine	Cost Effectiveness ($/ton)
Engine Replacement	2000, Transit Bus	$30,000	2.0 g/hp-hr 12 year life	$6,000 annualized $58,000 1-year
	2000, Diesel Aerial lift, 175 hp	$11,000	4.5 g/hp-hr 12 year	$17,000 annualized $173,000 1-year
	2000, Diesel Forklift, 175 hp	$11,000	4.5 g/hp-hr 12 year	$12,000 annualized $124,000 1-year
	1995, Diesel Forklift, 175 hp	$11,000	4.5 g/hp-hr 7 year	$5,000 annualized $31,000 1-year
Hybrid-electric	2003, Transit Bus	$150,000	-25% 12 years	$75,000 $750,000

The transit bus example represents close to a best-case scenario for an on-road project because transit buses have high activity rates within the nonattainment area and so provide a larger source of potential emissions reductions.

The comparison between the projects replacing an off-road engine (costing $11,000 as averaged in Carl Moyer program) with a Tier 2 engine (typical certification values for a Tier 2 engine shown in Table 4-3) is that a forklift is projected to operate 1,700 hours per year compare to only 384 hours for an aerial lift. So the forklift provides considerably more emission reductions than an aerial lift and is therefore a more cost effective project. Replacing older (as shown for a 1995 forklift in Table 4-3) engines also yields greater emission reductions, but the project length should be shorter because older engines would not be projected to last as long.

The hybrid electric bus example uses a relatively high cost of $150,000 per bus because this technology is still in a development phase and does not yet benefit from economies of scale. This type of project also suffers because the technology must be applied to new vehicle

purchases and cannot be easily retrofitted on older higher emitting vehicles. Lower costs, below $30,000 incremental cost per vehicle, would be needed before this technology is eligible for funding. Not calculated into the cost are the lower fuel costs (up to $4,000 per year per bus) and possibly lower maintenance costs due to steady-state engine operation of a hybrid-electric drive train.

CNG/LNG engine replacement can be used as either a new vehicle purchase or engine replacement, but it can be difficult to estimates the cost of a typical CNG/LNG program. For instance, infrastructure costs are often included in engine replacement programs raising the total cost of the project. New vehicle/equipment purchase can often be a low cost compared to purchase of a higher emitting vehicle, but engine replacement can be a much higher cost because of the need to replace the entire fueling system in addition to the engine. CNG/LNG engines currently meet lower emission standards than even the lowest emitting diesel engines, so the added emission reductions may justify the higher cost of infrastructure or engine replacement. Also, on an equivalent energy basis the cost of CNG/LNG is typically much lower than diesel, so owner/operators may be willing to absorb some of the additional capital cost.

4.3   ENGINE RETROFITS

Each retrofit option must be viewed in terms of the application applied and the best information available in terms of cost. The cost effectiveness estimates provided in Table 4-1 reflect reported estimates if available, but these reports may not reflect typical projects likely to be proposed. A summary of emission reduction retrofit cost effectiveness calculations are provided in Table 4-4.

The data for water injection and humid air intake engine retrofit methods are those reported by vendors or public information about projects involving marine vessels. The examples given in Table 4-1 were for ferries, which provides a best-case scenario for emission reduction because ferries have high activity rates (up to 4,000 hours per year) and high base emissions levels. Therefore the cost effectiveness estimates for this method are the best possible, which explains why this method appears to have the lowest cost effectiveness estimates. These techniques have not been suggested for use with other types of off-road or on-road engines perhaps because marine engines operate at more steady-state conditions.

The fuel injection method is currently only verified for on-road vehicles so the cost effectiveness for this approach is provided only for an on-road vehicle retrofit.

EGR retrofits are a funded TERP project, so the cost effectiveness estimates were taken from the TCEQ report. Vendors indicate that the cost of subsequent retrofits may be less. Because the EGR retrofit is not a yet verified project, perhaps the added cost to TERP would be to provide sufficient data for verification. Therefore, TERP provides support to vendors in the verification process to encourage early adoption of new technologies while maintaining cost effective emission reductions.

SCR retrofits have typically been used on stationary sources with steady-state loads, and application on on-road and off-road mobile sources must address the need for transient loads.

The cost used in this comparison was about $115/kW installed power, higher than vendor claims but within the range of public reports including the TERP funded project. The range of cost effectiveness for the off-road projects (aerial lift and forklift) shown in Table 4-4 brackets that claimed for the TERP project for retrofit of excavators at $12,000 annualized and $56,000 for the 1-year cost effectiveness.

Table 4-4. Sample engine retrofit projects situations for cost effectiveness analysis.

Project	Sample Vehicle\Equipment	Cost (per gallon)	Retrofit Effect	Cost Effectiveness ($/ton)
Engine Injection	2000, Transit Bus	$13,000	-25% 5 year life	$12,000 annualized $56,000 1-year
Lean NOx Catalysts	2000, Transit Bus	$10,000	-25% 5 year life	$10,000 annualized $43,000 1-year
SCR	2000, Transit Bus	$30,000	-80% 5 year life	$9,000 annualized $41,000 1-year
	2000, Diesel Aerial lift, 175 hp	$15,000	-80% 5 year life	$19,000 annualized $87,000 1-year
	2000, Diesel Forklift, 175 hp	$15,000	-80% 5 year life	$7,700 annualized $35,000 1-year

Other technologies reviewed here that may not be currently eligible for TERP funding but include technologies certified, verified, or have been funded in other programs similar to TERP.

Turbines are naturally low emission power sources, but work best when operated at higher steady-state loads and is probably best suited to replace a diesel generator set. Turbines are marketed as engines that last longer with less maintenance than diesel engines. For mobile sources, the only application of turbines that has been marketed is as the power source for a hybrid-electric transit bus. The sample projects in Table 4-5 demonstrate that the cost effectiveness turbines improves with higher use engines as with a mobile generator that is operated at 3 times the typical average annual usage. Using a turbine in a bus requires a hybrid-electric design because turbines cannot effectively follow the road load, but the high cost of hybrid-electric buses (assumed here to be $150,000) makes it difficult to justify the use of a turbine hybrid-electric bus. Also, turbines are not typically as fuel efficient as diesel engines.

Electrification of mobile equipment, forklifts, have been funded under the Carl Moyer program where Carl Moyer project cost effectiveness are reported in Table 4-1. A sample of electrification projects that might be considered under the current (diesel-only) or expanded (LPG or other spark-ignition engines) definition is shown in Table 4-5. The cost effectiveness range shown is similar to those listed for the Carl Moyer program.

Beginning with model year 2004, spark-ignition engines must meet a lower emission requirement that will likely lead to the use of three-way catalysts, but many off-road spark-ignition engines could apply this technology earlier or be retrofit with such devices and is very cost effective. Many on-road heavy-duty spark-ignition engines now meet lower emission standards than required and so offer potential emission reductions, but engine manufacturers typically do not offer retrofit or engine replacement.

Table 4-5. Sample engine replacement projects situations for cost effectiveness analysis.

Project	Sample Vehicle\Equipment	Cost (per gallon)	Retrofit Effect	Cost Effectiveness ($/ton)
Turbine	2000, Transit Bus Hybrid-Electric*	$200,000	0.56 g/hp-hr 12 year life	$29,000 annualized $290,000 1-year
	2000, Diesel 100 hp Generator Default 338 hrs/yr	$50,000	0.75 g/hp-hr 12 year life	$31,000 annualized $310,000 1-year
	2000, Diesel 100 hp Generator 1000 hrs/yr	$50,000	0.75 g/hp-hr 12 year life	$10,000 annualized $104,000 1-year
Electrified Forklifts	2000, LPG Forklift, 100 hp	$12,000	0 g/hp-hr 5 year life	$4,000 annualized $19,000 1-year
	2000, Diesel Forklift, 100 hp	$12,000	0 g/hp-hr 5 year life	$9,600 annualized $44,000 1-year
	2000, Diesel Forklift, 100 hp	$55,000	0 g/hp-hr 5 year life	$44,000 annualized $201,000 1-year
Spark-ignition TWC Retrofit	2000, LPG Forklift, 100 hp	$3,000	-90% 5 year life	$1,100 annualized $5,000 1-year
	2000, LPG Aerial lift, 100 hp	$3,000	-90% 5 year life	$3,000 annualized $15,000 1-year

* Combines use of a turbine (0.75 g/hp-hr NOx) with a hybrid electric drivetrain (-25% fuel consumption).

5.0 EMISSION INVENTORY SUMMARY

The emissions inventory presented here was the best information readily available from the State Implementation Plan (SIP) and TCEQ staff for the nonattainment areas of Houston-Galveston (HGA) and Dallas-Ft. Worth (DFW) (TNRCC[1,2]), the two areas receiving the most attention from the TERP. In addition, an initial attempt was made to estimate the emission inventory eligible for the Texas Emission Reduction Plan (TERP) funded projects.

Onroad emissions are presented in two formats produced from either the MOBILE5 or MOBILE6 models. At the time of the SIP development, the only emissions model available from EPA was the MOBILE5 model, but EPA has since released a new version of the on-road emissions model called MOBILE6. The modeling using MOBILE6 has not been finalized, so the results presented here are considered interim, but they provide an understanding of the likely effect the move to MOBILE6 will have on the emissions inventory for these two nonattainment areas. General estimates using MOBILE6 were available for most Texas counties using a modeling approach that closely approximates the SIP development of the onroad emissions inventory (TCEQ[3]). The SIP on-road emission inventory development relies on a link level analysis (where links are short road segments), and the approximate analysis used broad road classifications. A link level analysis using MOBILE6 was prepared for Houston (TTI[4]); however not yet completely vetted through the SIP process with the next revision to be performed as part of the mid-course review to be completed by May 1, 2004), so the approximate analysis could be compared with the more accurate link level analysis for HGA and show that the approximate approach closely predicts the link level approach.

The nonroad estimates for these two nonattainment areas relied on the NONROAD model for most equipment categories; and individual survey estimates for commercial marine, locomotive, and aircraft emissions. The NONROAD emissions model, currently available in draft form on the NONROAD web page at http://www.epa.gov/otaq/nonrdmdl.htm, describes most types of nonroad equipment. At the time of the SIP development, the version of the NONROAD model available is still the most recent version, dated June 2000. However, EPA has released a new version of the NONROAD model for use by State and Local air quality officials containing significant revisions in emissions estimates from earlier versions. The NONROAD includes both emission factors and default county-level population and activity data. For estimates in the two nonattainment areas, Texas modified the airport ground support and construction and mining population and activity estimates used in NONROAD to reflect more detailed local estimates.

We have used the SIP inventory to estimate the NOx emissions currently eligible for Texas Emissions Reduction Plan (TERP) according to the guidance published in October 2001, called "TERP-eligible" (TNRCC[5]). For this interim report, the TERP-eligible NOx emissions were estimated using eligibility criteria outlined by the TERP guidance and the results from the MOBILE6 and NONROAD models. This guidance restricts funding to diesel equipment above 50 hp or highway vehicles greater than 10,000 lbs gross vehicle weight rating (GVWR), where Class 2b trucks and vans are heavy-duty vehicles of 8,500 – 10,000 lbs GVWR.

For onroad emissions, MOBILE5 (the model used in the SIPs) only distinguished between heavy-duty (greater than 8,500 lbs GVWR) and light-duty, so the emissions for diesel vehicles

greater than 10,000 lbs were not estimated specifically. The TERP- eligible NOx emissions for onroad emissions were derived from the most accurate modeling using the results generated by the MOBILE6 model because this model did distinguish between more vehicle types including the cut-off for TERP-eligibility of 10,000 lbs GVWR.

For nonroad emissions, NONROAD provides emission estimates by category and by engine power, so the TERP eligible criteria could be applied to estimate the fraction of the SIP inventory eligible for TERP funding. Diesel (also called compression-ignition) powered equipment and those powered by engines greater than 50 hp can be determined unique of other nonroad equipment. ENVIRON performed modeling using the NONROAD model using input files that closely mirrored the modeling used in preparation of the SIP inventory to determine the fraction of nonroad emissions associated with diesel equipment and the fraction of greater than 50 hp diesel equipment emissions. The ENVIRON-determined fractions were applied to the SIP inventory to produce the estimate of TERP-eligible nonroad NOx emissions.

Several initiatives in either or both of the nonattainment areas addressed in this report compete with the TERP for projects to reduce emissions. In addition to the TERP, the SIP expects emission reductions from voluntary and statutory programs, and TERP eligible projects have typically been the most cost effective option and so become the choice for generating emission reduction credits to offset other requirements. In the Houston-Galveston nonattainment area, railways and push boat operators have signed voluntary commitments to reduce emissions that might otherwise be TERP-eligible. Congestion Mitigation and Air Quality (CMAQ) transportation dollars may fund onroad heavy-duty diesel vehicle projects and is a central theme of the Voluntary Mobile Source Emission Reduction Program (VMEP) outlined in the Houston-Galveston SIP. The VMEP also encourages voluntary emissions reductions from nonroad sources distinct from those funded by TERP. Companies meeting stationary sources requirements and airport ground support requirements may seek to create or buy emission credits or offsets from TERP-eligible sources.

5.1 HOUSTON-GALVESTON NONATTAINMENT AREA MOBILE SOURCE EMISSION INVENTORY

The Houston-Galveston Nonattainment Area consists of 8 counties: Brazoria, Chambers, Fort Bend, Galveston, Harris, Liberty, Montgomery, and Waller. The Texas Commission on Environmental Quality (TCEQ), formerly known as the Texas Natural Resources Conservation Commission (TNRCC), adopted a full State Implementation Plan (SIP) revision Houston/Galveston nonattainment area (HGA) in December 6, 2000 with additional minor revisions and clarification on September 26, 2001. The SIP calls for significant NOx emission reductions from all emission sources to bring the area into attainment by 2007. A SIP revision, called a mid-course correction, is due in spring 2004.

The Voluntary Incentive Program listed in the HGA SIP on September 26, 2001 indicated that Senate Bill 5 (which was the enabling legislation for the TERP) would be responsible for sufficient emissions reduction to "to replace the emissions lost by removal of the construction equipment operating use restriction and the accelerated purchase requirements" and to address a portion of the gap between the necessary emission reductions and those specifically outlined in the SIP.

The nonroad emission inventory was developed in large measure using local activity estimates including construction and mining equipment, commercial marine, locomotive, aircraft, and airport support equipment. The emission estimates for the remaining categories were developed using the draft NONROAD model or adjusted from earlier estimates. Table 5-1 provides the emissions used in the HGA SIP and is shown graphically in Figure 5-1.

Table 5-1. 2007 nonroad emissions in HGA.

Nonroad Category	VOC (tpd)	NOx (tpd)	TERP Eligible NOx (tpd)
Construction and Mining	5.5	32.1	31.2
Ocean-Going Vessels	0.9	30.1	0.0
Industrial	4.6	15.0	10.0
Agricultural*	1.8	12.9	12.0
Locomotive	1.1	12.1	*0.0*
Aircraft	4.4	7.4	*0.0*
Push Boat	0.2	7.3	*0.0*
Airport Ground Support	1.3	6.0	*0.0*
Commercial	14.6	5.1	2.8
Harbor Vessels	0.1	4.2	3.1
Recreational Marine	25.6	2.3	0.5
Commercial Fishing Boats	3.0	2.2	2.2
Lawn and Garden	41.2	1.2	0.3
Logging	0.0	0.5	0.5
Total	**104.8**	**138.2**	**62.6**

* More recent versions of the NONROAD model indicate that this category is less important than it appears in the SIP inventory.
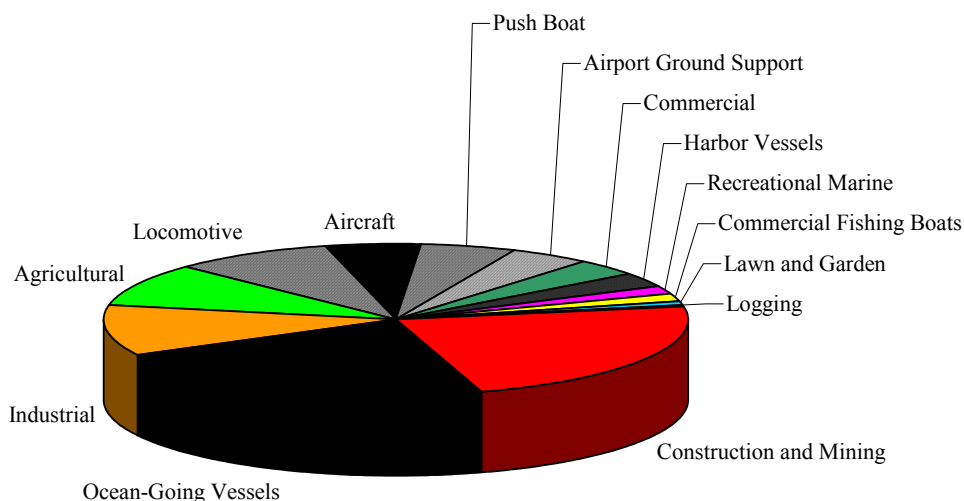
Figure 5-1. Houston-Galveston nonroad NOx emission by category.

In order to determine the available emissions for TERP funding, several exclusions were made by category for ineligibility, impracticability, or other reasons. Ocean-going Vessels (OGV) emissions were deemed impractical because such ships visit many ports, so the activity within

the Houston-Galveston area is a small fraction of annual activity. Likewise aircraft engines are considered an impractical source for emission control programs. Both ocean-going vessels and aircraft are considered to be unavailable for TERP funding, so are blacked-out in Figure 5-1. Airport ground support equipment is under separate agreements as part of the SIP to reduce their emissions. Since the time of the SIP approval, the large railways and push boat (barge) operators have signed agreements to provide voluntary emission reductions for the VMEP, so may be less inclined toward using the TERP funding. The harbor vessel category includes the Bolivar ferries (responsible for 1.1 tpd of NOx) that will be applying emission controls funded through the CMAQ program. These categories that are engaged in voluntary emission reduction programs are crosshatched in Figure 5-1 because these sources are eligible for TERP funding but are participating in other emission reduction programs.

The onroad emissions inventory is described in Tables 5-2 and 5-3 using MOBILE5 (the SIP inventory), MOBILE6-link level (most likely estimate of the mid-course review revision), and MOBILE6-approximate (only inventory available for Dallas-Ft. Worth). Table 5-2 describes how the predicted emission inventory is expected to change when MOBILE6 is used where light-duty vehicle (LDV) NOx emissions will likely be lower while heavy-duty vehicle (HDDV and HDGV) emissions will not change much. Table 5-3 indicates that the approximate method is comparable to the more detailed link level emission inventory. With MOBILE6, it is possible to distinguish between heavy-duty diesel vehicles below 10,000 lbs GVWR (called Class 2b) from other heavy-duty vehicles as indicated.

Table 5-2. HGA 2007 highway emissions comparison between MOBILE6 and MOBILE5.

Vehicle Type	MOBILE6 (link level)		MOBILE5 (SIP)	
	VOC (tpd)	NOx (tpd)	VOC (tpd)	NOx (tpd)
LDV	76.0	69.9	61	100.9
HDDV	2.3	60.0	10	65.5
HDGV	4.1	16.1	5	13.1
Total	**82.4**	**146.0**	**76**	**179.5**

Table 5-3. HGA 2007 highway emissions comparison between link level and approximate estimates (TERP-eligible NOx emissions equal 54.2 tpd).

Vehicle Type	MOBILE6 (link level)		MOBILE6 (approximate)	
	VOC (tpd)	NOx (tpd)	VOC (tpd)	NOx (tpd)
LDV	76.0	69.9	73.5	69.8
HDDV (HDDV2b)	2.3 (0.3)	60.0 (5.8)	2.3 (0.3)	53.6 (6.3)
HDGV	4.1	16.1	0.3	16.1
Total	**82.4**	**146.0**	**79.6**	**139.4**

The TERP eligible emissions are estimated to be 116.8 tpd for Houston-Galveston including both onroad and offroad emission sources. The most likely additional emission sources not currently eligible are heavy-duty onroad and off-road gasoline engines, which could provide additional emission reduction projects.

5.2 DALLAS-FT. WORTH NONATTAINMENT AREA MOBILE SOURCE EMISSION INVENTORY

The SIP for the Dallas-Ft. Worth Nonattainment Area, comprising the counties of Dallas, Tarrant, Denton, and Collins (TNRCC[6]), supplied the information for the nonroad emission inventory as shown in Table 5-4 and Figure 5-2. The corresponding VOC emissions were not readily available.

Table 5-4. 2007 DFW nonroad emissions (VOC information was not readily available).

Nonroad Category	NOx (tpd)	TERP Eligible NOx (tpd)
Construction and Mining	45.0	43.1
Industrial	10.7	4.7
Agricultural	0.7	0.7
Locomotive	8.2	*0.0*
Aircraft	14.9	0.0
Airport Ground Support Equipment	12.3	0.0
Commercial	2.4	1.3
Recreational Marine	1.3	0.3
Lawn and Garden	0.3	0.1
Other	4.0	?
Total	**99.8**	**50.2**
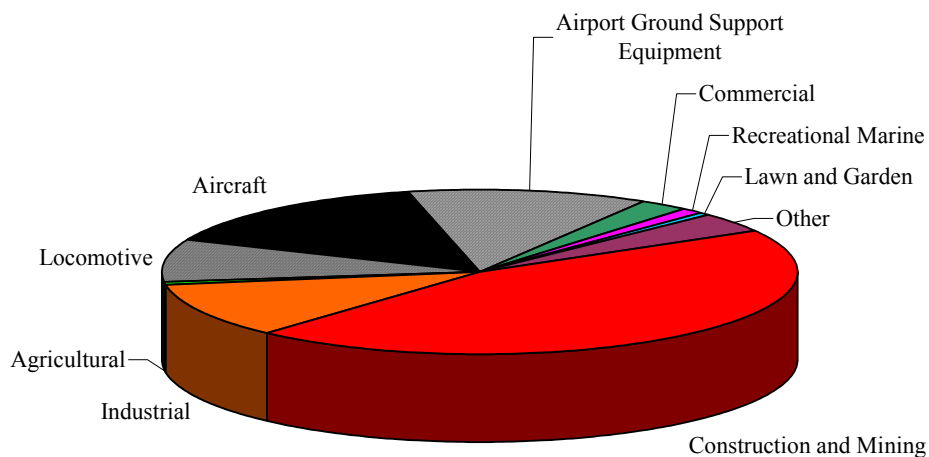
Figure 5-2. Dallas-Ft Worth nonroad NOx.

For the reasons described for Houston, aircraft and airport ground support equipment were deemed impractical for emission controls. Railways have not signed up for voluntary emission reductions in the Dallas-Ft. Worth area, but line haul engines comprise the majority of activity (~85%) and spend a low fraction of time within the DFW nonattainment area. In the SIP documentation, a category was listed as "other" and not well described; it could either be a nonroad mobile or area (stationary) source, so it was ignored as a category available for TERP funding.

Link level MOBILE6 estimates were not yet available for Dallas but approximate estimates using MOBILE6 were available and are shown in Table 5-5. As with Houston-Galveston, the light-duty NOx emissions are predicted to be much lower using MOBILE6 compared with MOBILE5, however heavy-duty vehicle emission were projected to be higher. Overall MOBILE6 projects lower NOx emissions.

Table 5-5. DFW 2007 highway emissions comparison between MOBILE6 and MOBILE5 (VOC information unavailable or inconsistent) (TERP-eligible NOx emissions equal 65.1 tpd).

Vehicle Type	MOBILE6 (approximate) NOx (tpd)	MOBILE5 NOx (tpd)
LDV	85.2	158.7
HDDV	74.4	59.1
(HDDV2b)	(9.3)	(not available)
HDGV	23.8	15.1
Total DFW	**183.5**	**232.9**

The TERP eligible emissions total 115.3 tpd for Dallas-Ft. Worth including both onroad and offroad emission sources. The most likely additional emission sources not currently eligible are heavy-duty onroad and off-road gasoline engines, which could provide additional emission reduction projects.

5.3 SUMMARY

The total mobile source (onroad and offroad) NOx emissions inventories for Dallas-Ft. Worth (DFW) and Houston-Galveston (HGA) and the emission inventory available for TERP funding are remarkably similar between the two regions. DFW was projected to have more onroad and less nonroad NOx emissions than for HGA. DFW was estimated to be 115 tpd NOx eligible for TERP funding out of 283 tpd of mobile source NOx emissions. HGA was estimated to be 117 tpd NOx eligible for TERP funding out of 284 tpd of mobile source NOx emissions.

Opportunities for additional benefits exist by expanding the definition of TERP-eligible equipment to include all (Class 2b; GVWR of 8,500 to 10,000 lbs.) heavy-duty highway vehicles and smaller diesel and spark-ignition (especially larger engines such as used in forklifts) engine emission reductions. These areas ignored by the TERP present TCET an opportunity to fund additional emission reductions and to demonstrate emission reduction technologies.

For Houston, an additional 34 tpd or a 30% increase over the 116.8 tpd of currently TERP-eligible NOx emissions becomes available for reductions.

> HDDV Class 2b = 5.8 tpd NOx
> HDGV all classes = 16.1 tpd NOx
> Nonroad small diesels = 3.1 tpd NOx
> Nonroad spark-ignition = 8.8 tpd NOx
> (Mostly Industrial and Commercial Equipment types)

For Dallas, and additional 43.5 tpd or a 38% increase over the 115.3 tpd of currently TERP-eligible NOx emission becomes available for reductions.

> HDDV Class 2b = 9.3 tpd NOx
> HDGV all classes = 23.8 tpd NOx
> Nonroad small diesels = 2.4 tpd NOx
> Nonroad spark-ignition = 8.0 tpd NOx
> (Mostly Industrial and Commercial Equipment types)

For smaller off-road diesels, the applicable technologies may be limited to relatively low capital cost approaches because the total emissions produced per engine may be low increasing the cost per emissions reduced. Certainly fuel measures (reformulated diesel and fuel/water emulsions) described in subsequent chapters would be applicable to these engines, but other retrofit devices may be less applicable. EPA[7] predicts that smaller diesels are comprised largely of naturally aspirated indirect-injection engines (as opposed to turbocharged direct-injection engines commonly used in larger on-road and off-road diesel engines), which may limit the number of technologies that can be applied to reduce NOx emissions from these engine types.

For smaller on-road heavy-duty (8,500 to 10,000 lbs GVWR) diesel vehicles, there is no fundamental technology difference between these and large currently TERP-eligible vehicle\engine combinations. The current limitation of TERP funding arbitrarily excludes these vehicle types.

For off-road or on-road spark-ignition, three-way catalysts are marketed for retrofit reducing emissions up to 90%. The Texas and now Federal emission standards for call for new nonroad engines starting in 2004 to meet lower emission standards, however many existing engines not meeting these new emission standards will operate for many years to come but could be retrofit for lower emissions.

California ARB (http://www.arb.ca.gov/msprog/moyer/moyer.htm) has included retrofit or replacement of diesel engines used as a stationary source (to distinguish from mobile sources though not necessarily permitted stationary point sources) in the Carl Moyer program, which was the basis for the TERP. These semi-stationary sources could include irrigation pumps, generators, compressors, and other sources currently not eligible for TERP funding. These diesel engines are not necessarily different than those used to power mobile sources that are eligible for TERP funding, so emission reduction projects could be similar to those already funded by TERP. For emission inventory purposes, these diesel engines are typically called area sources and are combined under fuel combustion with smaller boilers and similar uses of

fuel oil. A separate estimate of the emissions associated with stationary diesel engines may not be readily available.

6.0 SUMMARY AND RECOMMENDATION

Technologies exist to reduce diesel engine emissions including cleaner fuel options, engine\vehicle replacement, and retrofit of existing engines. Several fuel option exist that provide emission reductions from on-road vehicles and off-road equipment including funded TERP projects for fuel/water emulsions as well as other yet unfunded and underdeveloped options for additional diesel fuel reformulation. The most prevalent TERP-funded project, as well as the most effective under the analogous California Carl Moyer program, is to perform early retirement of vehicles or equipment or replace current engines with cleaner diesel or CNG/LNG engines. Retrofit options for current equipment include applying additional equipment to humidify the intake air, modify fuel injection timing with additional particulate traps, applying exhaust gas recirculation (EGR), lean NOx reduction catalysts, and selective catalytic reduction. Additional retrofit options applying nascent technologies of NOx adsorbers or plasma NOx reduction catalysts may become available in subsequent years.

A summary of the available technology options reviewed in this report is provided in Table 6-1, including the current status of technology options. The status is provided in three forms; "Available" where vendors are offering verified technology options for sale, "Near-Term" where vendors have developed and demonstrated the technology but is yet unverified or does not have official approval to claim emission reduction credits, and "Developing" where technologies still require significant development. In some cases the technology has been developed for some vehicle or equipment applications but not all applications. The "Near Term" and "Developing" technologies could be candidates for the TCET projects where vendors and owner/operators of vehicles and equipment would welcome additional development assistance.

Table 6-1. Emission reduction technologies emission reduction potential, level of feasibility, and verification status.

Technology	NOx Reduction Potential (Accepted or Vendor Claim)	Available	Near Term	Developing
Fuel Measures				
Fuel reformulation (e.g. cetane enhancers)	Up to 5% (Beyond Texas LED)		X	
Fuel reformulation Fischer-Tropsch	Up to 14 % (Beyond Texas LED)		X	
Fuel-water emulsion	14% - 16% (ARB) ~13% Hwy (in 2007) ~20% Nonroad (in 2007)	X		
New Engine, Vehicle, or Repower				
Clean Diesel	Up to 80% Highway Up to 50% Nonroad	X		
CNG\LNG	Better than Clean Diesel option	X		
Hybrid System	Up to 40%	X	X	
Engine Retrofit or Aftertreatment				
Water Injection	Up to 50% reported		X	X
Humidified Air	Up to 50% reported		X	X
Injection retard (with PM Control)	~ 25%	X		
Turbocharger (with aftercooling)	NA		X	
Manifold and port designs	NA		X	
Combustion chamber design	NA		X	
Fuel-injection systems	NA		X	

Technology	NOx Reduction Potential (Accepted or Vendor Claim)	Available	Near Term	Developing
Exhaust gas recirculation (EGR)	Up to 50%		X	
Lean NOx catalyst	20 – 35%	X	X	
NOx adsorber	Up to 90%			X
Selective Catalytic Reduction (SCR)	Up to 90%		X	
Plasma Reduction	Up to 90%			X
Other Technologies				
Turbine engines	Up to 90% (50% cleaner than diesel)		X	
Electrification	100%	X		
Fuel Cells or Solar Cells	Up to 100%		X	
Spark-ignition with 3-way catalyst	~ 90%	X		

The emission reductions that can be claimed for any technology or project will depend upon what EPA determines appropriate and relies on a official verification of the technology used. However the verification of many of these technologies has lagged because the verification process is cumbersome and costly. For instance, EPA has not verified any NOx reduction technologies, though it has published best estimates for the emission reductions from the use of cleaner fuel options. EPA has verified to date only particulate control technologies. California ARB has verified an injection modification control technology and is currently reviewing and provided initial approval for a lean NOx reduction catalyst to provide NOx emissions reductions (but for a limited engine manufacture/series and use). TERP has funded an EGR retrofit project that does not currently have verification status, but presumably will have verification by its conclusion. Because retrofit options are burdened by the verification process, the most straight-forward and therefore the most widely employed NOx reduction methodology is to accelerate the turnover of diesel engines to those meeting significantly lower emission standards.

The cost and cost effectiveness for these technologies was determined using the official TERP method, an annualized approach where the cost of the project is converted to an annual cost benefit over the life of the project divided by the annual benefit, or as a 1-year cost effectiveness where the total cost of the project is divided by the benefit in the attainment year. These two metrics are used because the technologies may rank differently depending on the time scales of the emissions reductions. The technologies reviewed in this report that could be funded under TERP have a range of annualized (i.e., over the life of the project) cost effectiveness from $1,000 to well over the $13,000 per ton of NOx reduced limit for TERP eligibility. Typically, the annualized cost effectiveness for TERP projects has been about $10,000 per ton of NOx reduced while the comparable Carl Moyer program has experienced lower cost effectiveness in the range of $3,000 to $6,000 on average. An alternative 1-year cost effectiveness (where the entire cost is divided by the emission reduction in the attainment year) is useful for determining the total cost of an air quality goal. Best estimates from the Carl Moyer program indicate that the 1-year cost effectiveness method has yielded projects that have 1-year cost effectiveness values of about $19,000. The Sacramento SECAT program readily funds projects with 1-year cost effectiveness of $50,000/ton. Off-road projects have tended to be more cost effective than on-road projects because base emissions rates for off-road engines is higher than those used in on-road vehicles resulting in greater actual emission reductions.

An emission inventory summary presented the NOx emissions likely eligible for TERP funded projects, and additional emission reductions that could be derived from sources currently ineligible for TERP funding but where TCET could provide assistance. The emission inventories were derived from the State Implementation Plans for the Houston-Galveston (HGA) and Dallas-Ft. Worth (DFW) nonattainment areas for off-road engines and according to the best information using the new MOBILE6 model for on-road vehicles. In HGA, 117 tons per day (tpd) of NOx emissions (54 tpd from heavy-duty on-road diesel vehicles above 10,000 pounds gross vehicle weight and 63 tpd from off-road diesel engines above 50 horsepower) are eligible for TERP funded projects. By expanding the definition of TERP-eligible to include other heavy-duty diesel vehicles (6 tpd), heavy-duty gasoline vehicles (16 tpd), smaller off-road diesel engines (3 tpd), off-road spark-ignition engines (9 tpd), and stationary internal combustion engines, the available emissions in HGA for emission reduction projects can be increased by more than 30%. Similar estimates for DFW show that the currently TERP eligible NOx emissions are 115 tpd and additional sources can increase the available emissions by more than 40%. TCET could therefore consider technologies that apply to these sources, (smaller on and off-road heavy-duty diesels and large spark-ignition off-road engines) which are ignored by other emission reduction programs.

Opportunities for TCET and recommendations for improvement of the TERP and other incentive programs include adding verification assistance to "jump-start" significant emission reduction technologies, lower the minimum emission reduction for retrofit to below 30% reduction, and expand the eligible emission sources to include more on-road and off-road equipment types.

TCET and TERP could assist various technologies by providing funding to assist in the verification process. In the past funding cycle, TCET has provided this type of funding to assist a lean NOx reduction technology (which subsequently received California verification), and TERP has funded a large project for an EGR retrofit project, which must include verification as an overall goal of that project. Technologies developing to meet the 2007 on-road diesel engine emission standards to reduce NOx emissions by up to 90% (including selective catalytic reduction (SCR), NOx adsorbers, or plasma catalytic reduction) provide additional opportunities to assist in developing retrofit options. These technologies that are used to meet new engine emission standards are likely also to be the most cost effective retrofit technologies to promote emission reductions from existing engines and could benefit from resources to enable their development and verification.

Two additional emission reduction technologies exist, but would be declared ineligible under the TERP requirement that such technologies must reduce emissions by more than 30%: fuel injection modifications and lean NOx catalysts. These technologies have been verified by California, and so might reasonably be expected to obtain EPA verification and might be widely employed. If the 30% reduction minimum is not lowered, then these technologies would be effectively ignored and attention should shift to focus on technologies expected to be eligible for funding.

Currently available technologies may be applied to vehicle or equipment that is not currently eligible for TERP funding. These include smaller diesel engines, Class 2b (gross vehicle weight ratings of 8,500 to 10,000 lbs) vehicles, and stationary diesel engines where the

technologies feasible for the currently eligible engine types could be applied to produce additional emission reductions.

Additional technologies could be considered under an expanded definition of eligible emission sources including California Carl Moyer projects for electrification of certain equipment types, use of fuel or solar cells for applicable equipment types, retrofit of uncontrolled spark-ignition engines with NOx reduction catalyst (such as are found on light-duty vehicles), and selective use of turbines instead of internal combustion engines. The expanded emissions sources would necessarily include Class 2b heavy-duty vehicles, smaller than 50 hp diesel engines, on and off-road spark-ignition engines, and stationary internal combustion engines.

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